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DESIGN OF A WATER-DISPOSABLE GLASS PACKAGING CONTAINER. PART I: PROTECTIVE OXIDE COATINGS FOR GLASSES BY CHEMICAL VAPOR DEPOSITION. PART II: MECHANICAL PROPERTIES OF WATER-SOLUBLE SODIUM SILICATE GLASSES. PART III. THE RATE OF DISSOLUTION OF SODIUM SILICATE GLASSES IN AQUEOUS SOLUTIONS

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DESIGN OF A WATER-DISPOSABLE

GLASS PACKAGING CONTAINER

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DESIGN OF A WATER-DISPOSABLE GLASS PACKAGING CONTAINER

Part I: Protective Oxide Coatings for Glasses by Chemical Vapor Deposition

Part II: Mechanical Properties of Water-Soluble Sodium Silicate Glasses

Part III: The Rate of Dissolution of Sodium Silicate Glasses in Aqueous Solutions

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were prepared by SAMUEL F. HULBERT, C. CLIFFORD FAIN, and MICHAEL J. EITEL
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FOREWORD

PACKAGING WASTES constitute a significant and growing fraction of the total solid waste load, and a major component of this total is the glass container.

In a study done for this agency, the Midwest Research Institute found that shipments of glass containers have grown from 20.2 billion units in 1958 to 29.4 billion units in 1966.¹ They projected a consumption rate by 1970 of 34.9 billion units and by 1976 of 45.7 billion units. During the period from 1966 to 1976 they expect the shipments of glass beverage containers to more than double, as nonreturnable containers account for a larger and larger share of the market.

We applaud the nationwide program by which glass container manufacturers are supporting recycling activities. Clearly, though, other avenues must be explored, including the concept of reducing solid wastes at the source--reducing the quantities of waste that will ultimately require storage, collection, transport, processing, and disposal.

Under the authority of the Solid Waste Disposal Act of 1965, amended by the Resource Recovery Act of 1970, research has been undertaken for the study and solution of problems caused by packaging wastes. The research work discussed in this report illustrates the innovative and imaginative approach being brought to bear on the problem. The development of a water-soluble glass container, presented in this three-part work, has high potential for promoting source reduction, and thereby improving the quality of our environment.

¹Darnay, A., and W. E. Franklin. The role of packaging in solid waste management, 1966--1976. Public Health Service Publication No. 1855. Washington, U.S. Government Printing Office, 1969. 205 p.

P R E F A C E

THIS REPORT was prepared by the Division of Interdisciplinary Studies, Clemson University, Clemson, South Carolina, under U.S. Public Health Service Research Grants UI-00651 and EC-00033.

The work reported in Part I was performed in fulfillment of the thesis requirements for the degree of Master of Science in Ceramic Engineering by Martin M. Cooper under the direction of Dr. C. Clifford Fain. The work reported in Part II was performed in fulfillment of the requirements for the degree of Master of Science in Materials Engineering by Charles Wesley Jennings under the direction of Dr. Samuel F. Hulbert. That reported in Part III was performed in fulfillment of the requirements for the degree of Master of Science in Ceramic Engineering by David Taylor Ballenger, also under the direction of Dr. Hulbert.

PART I

PROTECTIVE OXIDE COATINGS FOR GLASSES BY CHEMICAL VAPOR DEPOSITION

ABSTRACT

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A method of coating water soluble silicate glasses with oxide films by chemical vapor deposition was studied. The work represents the initial phase of a three year investigation to determine a feasible method of processing glass containers after use in order to relieve a source of solid waste currently reaching gigantic proportions nationally.

A detailed description of the system was provided to include coating equipment design features, input material requirements, and techniques of coating. Particular attention was given to key process control parameters such as temperature control, evaporation rates, and vapor transport procedures.

Coatings of silica, titania, and other oxides were readily obtained by pyrolytic decomposition of organic ester vapors. The reaction kinetics of selected materials were analyzed in terms of the process conditions used to derive them. For example, the effects of deposition temperature, carrier gas flow rate, reactant vapor concentration in the carrier gas stream, and substrate orientation were correlated with deposition rates and coating efficiencies.

High quality coatings of both silica and titania were obtained on soluble glass substrates by exercising proper judgment in the choice of process conditions to be used. Oftentimes the best coatings were obtained at the expense of longer coating times and lower efficiencies. The films produced, however, were found to be continuous, highly resistant to various forms of corroding media, and adherent to the surface of the substrate.

The titania films were most readily applied as uniform thin films at a growth rate of approximately 6000 Å per hour between temperatures of 500° F - 800° F. It was determined that the film structures were readily controlled by proper attention to process parameters. The silica films were generally applied under more restricted conditions, typically between 1000° F - 1050° F at about 4000 Å per hour.

Both types of oxide coatings were found to produce undesirably high residual stress levels, primarily because of a mismatch of thermal expansion coefficients between the coating and the substrate. In addition, many coatings exhibited microstructural variability primarily caused by uncontrollable coating conditions such as poor control on vaporization and gas delivery processes, impurities, substrate surface variations, localized temperature fluctuations, and others. The variable coating microstructures in conjunction with high residual stress levels are believed to promote a generally higher defect level such as microcracks and pinholes, thus contributing to a premature breakdown of the continuous barrier under water attack. The fact that tentative investigations revealed a wide scatter in the times required for water to penetrate and dissolve a coated specimen tends to amplify this observation.

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PART I

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INTRODUCTION

The great natural resources of our nation have been ingeniously utilized by a resourceful people to create a vast industrial capability which today provides an expanding population with the highest standard of living on earth. This epic growth has been accompanied, however, by a constantly expanding quantity of material wastes emanating from our nation's communities. By virtue of the current magnitude of the problem we are now urgently compelled to find new methods to process or neutralize these wastes rather than simply digest or absorb them as in the past. Our people can no longer afford to ignore the effects of belching factory smoke, gaseous emissions from vehicles, foul liquid contaminants dumped into our streams, and solid wastes piled up at refuse dumps or discarded along our roadways, for to do so will subject much of our citizenry to potentially severe health hazards as well as contaminate the beauty of our national landscape.

Recent reports (1) indicate that the nation has already taken conclusive steps to control gaseous and liquid wastes. In contrast, however, it is pointed out that we are just beginning to focus our attention on the problems related to solid wastes. The Federal Government is now providing funds and leadership for research and planning programs to curb the undesirable effects of inadequate solid waste control. Essential to this effort is a method of processing incombustible, unreactive glass containers after use. The potential impact of such a development upon solid waste control may be readily visualized by considering that approximately 135 glass

bottles and jars are produced each year for every person in the United States. This amounts to about 27 billion glass containers per year (2).

This paper represents the initial segment of a projected three year study to formulate a method of reducing the source of glass container waste by utilizing a water soluble glass encapsulated in a thin, impervious coating which resists corrosion by the environments normally encountered by the glass packaging industry. After the consumer empties the container, the continuous physical barrier may be broken and the water soluble glass dissolved. It is anticipated that the decomposition could be made to occur gradually over several months' duration, as at a municipal refuse dump, or relatively rapidly, perhaps within several minutes, by adjustment of the chemical and physical parameters of the base glass and its overlay coating.

This paper describes the use of chemical vapor deposition processes for applying chemically inert metallic oxide coatings to soluble glass substrates. A detailed analysis of the method is presented and its potential feasibility for vitreous container waste control is discussed.

REVIEW OF LITERATURE

A. Solid Waste Control

The problem of solid waste control in our country is rapidly approaching critical proportions. This statement surprises many people, for generally speaking, the public is not aware that there is a problem. A vivid illustration of public apathy can be seen in the attitude toward the throw-away glass bottle which relieves the producer, distributor, and consumer of handling costs and inconvenience, but creates more burdens for refuse collectors. Unfortunately, most people are not even aware of the additional problems that have been created by this convenience item. The refuse collector is painfully aware of his increased burdens, however. The use of non-returnable glass bottles is increasing (3), and no immediate solutions are in sight, although some states have begun to introduce legislation (4) in an effort to curb their production.

It is estimated (5) that glass comprises five to ten percent by weight of all refuse ending up on municipal dumps. Of course, scrap glass represents a major solid waste problem because, unlike much refuse, it is non-degradable. In addition to being aesthetically objectionable, discarded glass containers may harbor rodents and catch other vermin. They may catch and hold water in which mosquitoes may breed and subsequently transmit malaria, yellow fever, dengue, mosquito-borne encephalitis, and filariasis (6).

At present, non-combustible glass containers can best be disposed of by sanitary landfill techniques. Obviously, this does not represent the complete answer, for convenient sites are not always available.

In a major effort to generate fresh approaches directed toward solution of the problem, the Federal Government passed the Solid Waste Disposal Act, which became law on October 20, 1965 (1). The Congress assigned responsibility for administering the Act to the Secretary of Health, Education and Welfare and to the Secretary of the Interior. It is interesting to note that similar legislation to combat water and air pollution has been in effect for twenty, and twelve years, respectively (1).

This work represents one facet of the total program which has been implemented in selected universities and industrial research facilities throughout the country.

B. Soluble Silicate Glasses

Glass containers are carefully formulated today to yield high chemical durability. The resistance which glass offers to various corrosive agents is a property of great practical significance, according to Morey (7). This eminent glass authority further points out that the chemical durability of glass is oftentimes the chief reason for its preference over competing materials. As an example, he cites the use of glass containers which are used in enormous numbers for the distribution of commodities ranging from milk to medicine to acids. In this respect, he concludes that the superiority of glass leaves it without a competitor.

Of course, the hypothesis of this paper requires that a vitreous container must be soluble in order to be readily eliminated after use. Thus, a water soluble glass, with satisfactory optical, mechanical and chemical properties for container use is required. Fortunately, a vast market exists today which makes use of water soluble glasses. Vail (8) discusses the diverse uses for these alkaline silicate materials, which may serve such purposes as adhesives, cleaners, cements, defloculants, and protective coatings.

Vail (9) points out that the largest quantity of soluble glass produced for the soluble silicate industry is the eutectic composition between sodium disilicate and quartz, which is readily dissolved by water in less than one hour. Potassium silicate glasses are also known to be readily soluble.

The properties of the alkali silicate glasses have been investigated, but generally the reasons were for scientific curiosity rather than to achieve any practical objective. Their properties tend to change continuously as a function of composition rather than show the abrupt type of discontinuity characteristic of heterogeneous crystalline systems. The solution rate depends primarily upon the ratio of alkali to silica in the glass (9).

The alkali silicate glass system would offer some inherent advantages if adopted for glass container production. As reviewed by Vail (8), sodium silicate solutions are now added to polluted waters, as a flocculant in the settling and filtering steps of water purification. At the same time, these solutions tend to form a thin film on the inside of water pipes which would protect them against water

corrosion. In addition, it is noteworthy to add that no adverse effects from potable waters which have been sodium silicate treated have been detected.

The production of alkali silicate glasses is simple and cheap. Most of the material made in this country is easily produced by firing mixtures of sand and sodium carbonate in open-hearth type furnaces of regenerative or recuperative design with gas or oil. The clear glass reaction product is then drawn directly into water to produce silicate solutions (9). The objective of this study is to use a similar procedure with the exception that the vitreous silicate will be made into a container and used prior to putting it into solution.

C. Coating Considerations

The choice of a coating mechanism for this work entailed the critical evaluation of several methods. These methods can best be categorized in terms of the size of the particles which are being used to produce the coating structure (10). They are (a) atomic species; (b) particulate material; and, (c) sheet material. On this basis, the following categories provide a reasonable framework for discussing coating methods.

1. Atomic species processes

- a. Vacuum evaporation
- b. Cathode sputtering
- c. Electrodeposition
- d. Chemical vapor deposition

2. Particulate material processes

- a. Flame and plasma spraying
- b. Enamelling
- c. Painting
- d. Trowelling

- a. Laminating
- b. Cladding

Chemical vapor deposition was used as the coating mechanism in this study because it is believed to be the best method for producing thin, impervious oxide coatings of desired quality. Lesser considerations governed the choice to some extent, such as potential adaptability to other materials systems, construction, maintenance, and production costs, and scale-up considerations.

Chemical vapor deposition may be defined (11) as a method of plating in which deposits are produced by heterogeneous gas-solid chemical reactions at the surface of a heated substrate. A volatile compound of the element or substance to be deposited is vaporized and the vapor thermally decomposed, or reacted with other gases or vapors at the substrate to yield non-volatile reaction products which deposit on the substrate as a coating.

Blocher (12) refers to chemical vapor deposition, vacuum evaporation, cathode sputtering, and electrodeposition as "molecular forming" processes, that is, they tend to build up coatings or deposits atom-by-atom upon a substrate. As a result, these processes have in common the potential of yielding dense deposits of controlled thickness and orientation. Such properties are essential for a sound protective coating.

Each of the molecular forming processes has its advantages and limitations. However, when these are analyzed, chemical vapor deposition comes out quite well by Blocher's comparisons. To illustrate, chemical vapor deposition is capable of yielding the greatest variety of products at rates of deposition equivalent to or

exceeding those of the other techniques. It has the greatest throwing power, that is, the ability to deposit uniformly on relatively complex shapes. Blocher regards the major drawback of chemical vapor deposition as the fact that the substrate must usually be heated to relatively high temperatures, which can lead to residual stresses in the deposit and subsequent mechanical failure provided the differential thermal expansion coefficients between the substrate and the coating are sufficiently high. The other techniques have the advantage of maintaining the substrate at ambient temperatures.

Accountius (13) regards chemical vapor deposition as still largely a laboratory operation, except in a relatively few instances. He states that the deposition of each material is unique, and in nearly every case, further study of the thermodynamics, kinetics, heat transfer, chemistry, and solid state phenomena are required to elevate chemical vapor deposition from the status of an art to that of a science.

In spite of its many unexplored facets at present, the process has evolved quite rapidly from a technological standpoint in the last fifteen years. One may gain an accurate idea of its recent growth by comparing the 1955 state-of-the-art survey entitled Vapor Plating (14) with its 1966 revision, Vapor Deposition (15), both prepared under the auspices of Battelle Memorial Institute, an organization which has spearheaded the bulk of fundamental and applied research that has gone into the field.

The use of chemical vapor deposition is already well entrenched in protective coatings technology. It is interesting to note, in fact, that the first significant

historical application of the technique grew out of a need for a protective coating material in the incandescent lamp industry in the last two decades of the nineteenth century (11). Sawyer and Man (16) deposited pyrolytic carbon, and Aylsworth (17) and deLodyguine (18) deposited metals onto carbon filaments. Unfortunately, this particular application was never very satisfactory because of the brittle carbon core, and interest in chemical vapor deposition as a coating tool soon subsided for several years.

Since 1935, however, several interesting applications of chemical vapor deposition have been devised to protectively coat metals, alloys, and non-metallic materials against erosion and abrasion, general corrosion, and high temperature oxidation. These have been reviewed by Krier (19). Countless materials are currently protected by siliconizing, chromizing, nitriding, and other like processes which make up a vast commercial endeavor. There are also a large number of research and development programs active today. Emanating from these programs are such developments as new silicide and aluminide coatings for the aerospace industry, pyrolytic carbon coatings for rocket nozzles and re-entry vehicle surfaces, and others. These coatings are usually chemically vapor deposited by pack cementation or fluidized bed methods, two sub-processes of chemical vapor deposition which hold high promise for future applications.

Another use of chemical vapor deposition has been recently discovered in the atomic energy field. Small spherical fuel particles such as uranium dioxide are coated with oxides or carbides by fluidized bed techniques to produce a dense, impervious barrier to fission products or other reaction products (20). The fission

product retention of these coatings has been found to be significantly low. Characteristically only a few parts per million (ppm) of Xe^{133} fission gas generated in neutron activation is released on post irradiation heating. As a primary result of this caliber of performance particulate fissionable material encapsulated in a vapor deposited coating is believed to have the potential for solving many problems in reactor technology.

Curiously, as mentioned previously, the molecular forming processes such as chemical vapor deposition have the ability to control the structure of a coating. For example, a coating may be made to exist in either a crystalline or amorphous form, or a combination of both, depending upon the proper selection of deposition parameters. Walton (21) explained the phenomena by pointing out that no orientation is produced when a single bond (i.e., an atom joined to a cluster by a single bond) is stable. Single bonds rather than multiple bonds occur provided the substrate temperature is low enough or the reactant gas incidence rate high enough. If, on the other hand, the supersaturation is low enough for multiple bonds to be stable, but not single bonds, an oriented deposit can result. Interpreted another way, if one is obtaining crystalline films on a given substrate, the process may be adjusted to yield amorphous or glassy films by increasing the deposition rate and/or decreasing the substrate temperature.

Several investigators have discussed whether amorphous films should be termed glasses. Secrist and Mackenzie (22) have proposed that there is no distinction, based upon their work. They compared the critical structure indicators

of amorphous silica prepared by conventionally cooling from a melt and from various deposition techniques and found no significant changes.

This exciting discovery means that glassy materials may be prepared by such processes as sputtering, vacuum evaporation, and chemical vapor deposition as well as by the classical method of cooling from a melt.

The concept has radically altered ideas on what substances are capable of forming glasses. Many oxides and non-oxides are capable of being made into glasses by the molecular forming techniques although most of them cannot be obtained as glasses in bulk form by cooling from a melt. Sinclair (23) states that essentially any material which can be deposited by the molecular forming processes can be made into amorphous or glassy films.

An amorphous film has inherent advantages for a coating application such as the one proposed in this paper. Sinclair (23) points out, for example, that glass films have no grain boundaries and are isotropic. For this reason, they are currently used extensively in the field of thin-film microelectronics as diffusion barriers to keep water and ionic contaminants from junctions.

On the other hand, Sinclair (23) points out that the properties of glass films are greatly effected by methods of preparation, techniques, and conditions. He illustrates the effect of impurities by stating that a monolayer of water absorbed onto a substrate surface, if incorporated into a 1000 Angstrom (A) silica film, would represent 0.5 mole percent of the composition. Additional water soluble surface contaminants such as sodium ions would have the dual effect of being impurity sources in their own right and also causes of increased water absorption

on the surface. He concludes the the predeposition cleaning procedure is very important.

Holland (24) generally takes a dim view of the feasibility of protecting glass surfaces by vapor depositing oxide films onto the substrate. Citing results from sputtering and vacuum evaporation techniques, he states that it is difficult to produce films completely free from pinholes. He also observes that only a limited range of film materials have suitable optical properties to allow their use.

Overall, the writer believes that selected oxide coatings, chemically inert to water and other corroding media, offer a splendid source of potential for research in the field of coating soluble glasses by chemical vapor deposition. The literature contains several references to work which has been recently accomplished in this area on relatively durable compositions. For example, thin titania films are now commonly applied to glass bottles after annealing primarily to impart a more effective scratch-resistant finish (25). The method involves the use of a volatile organic titanate which is easily pyrolyzed to effect the reaction. The resulting film is extremely thin and transparent and is said to impart a substantial degree of additional durability. The method is also applicable to the oxides of aluminum and zirconium (26).

Badger (27) has discovered that silica deposited on glass surfaces by treatment with ethyl orthosilicate or other alkoxysilanes, at a temperature between the melting point and the softening point of the glass, increases the chemical durability of the glass. The same system has been devised for aluminum oxide, deposited from

aluminum isopropoxide, and is said to work for any oxide which forms constituents of conventionally prepared durable glasses.

Mixed oxides may be deposited by using single oxide deposition processes and mixing the metal compounds in the plating atmosphere (28). Such procedures are readily adaptable to producing borosilicate glass coatings produced by the mixed vapors from ethyl orthosilicate and triethyl borate.

Several oxides have been coated sequentially onto a substrate to form composite layers (28). Such materials as silica, alumina, titania, and zirconia have been mentioned. This latter method would possibly offer advantages in minimizing the effects of pinholes and other growth defects.

CHAPTER III

OBJECTIVES OF RESEARCH

The objective of this research was to define the capabilities of chemical vapor deposition as a tool for coating soluble glass substrates with metallic oxide films. The work represents a segment of a projected three year study which will deal with methods of processing glass packaging containers after use. In order to accomplish the objective of this investigation, the research was divided into three phases, as discussed below.

The first phase involved the design and construction of a mechanism capable of depositing metallic oxide films from the vapor phase onto soluble glass substrates. The proper selection of equipment components and materials necessarily involved an extensive research effort and numerous calculations to assure that satisfactory coatings could be attained over a wide range of controlled conditions.

The second phase of the research effort was directed toward characterizing selected coatings in terms of various process parameters, as well as accumulating basic data designed to reveal the overall feasibility of the system's capability of performing its ultimate task by considering various pertinent properties of the composite produced.

The third phase of this work involved a critical assessment of the system investigated. Its basic limitations were discussed, and suggestions were given for possible improvements to be incorporated into the current facility.

EXPERIMENTAL PROCEDURE

A. Coating Apparatus Design

The vapor deposition apparatus designed and constructed for this study is shown schematically in Figure 1 and photographically in Figure 2. The choice of components was carefully screened to provide a system capable of depositing a wide spectrum of materials over a range of controlled conditions. At the same time, it was deemed advisable to maintain a simplified and straightforward design concept which can be ultimately tailored to scaled up production operations with minimum difficulty.

A mullite-lined tube furnace served as the reaction chamber for this investigation. The combustion tube, purchased from McDanel Refractory Porcelain Company, measured thirty-six inches in length. Its cross sectional dimensions were 2 1/4 inches inside diameter with a 1/8 inch wall thickness. The ends of the tube were readily closed off with rubber-gasketed aluminum doors supplied by the same company. O-ring compression seals were mounted on the doors to provide 1/4 inch gas tight lead-throughs for the entrance and exit of gases. Thermocouples and other control components were also introduced into the interior of the reaction chamber via the same type lead-throughs. The thermocouple wires extending through the double bore porcelain insulator tubing were sealed with epoxy cement to prevent gas leakage. The sealed door arrangement provided a gas tight system capable of being dynamically monitored or controlled during a coating run.

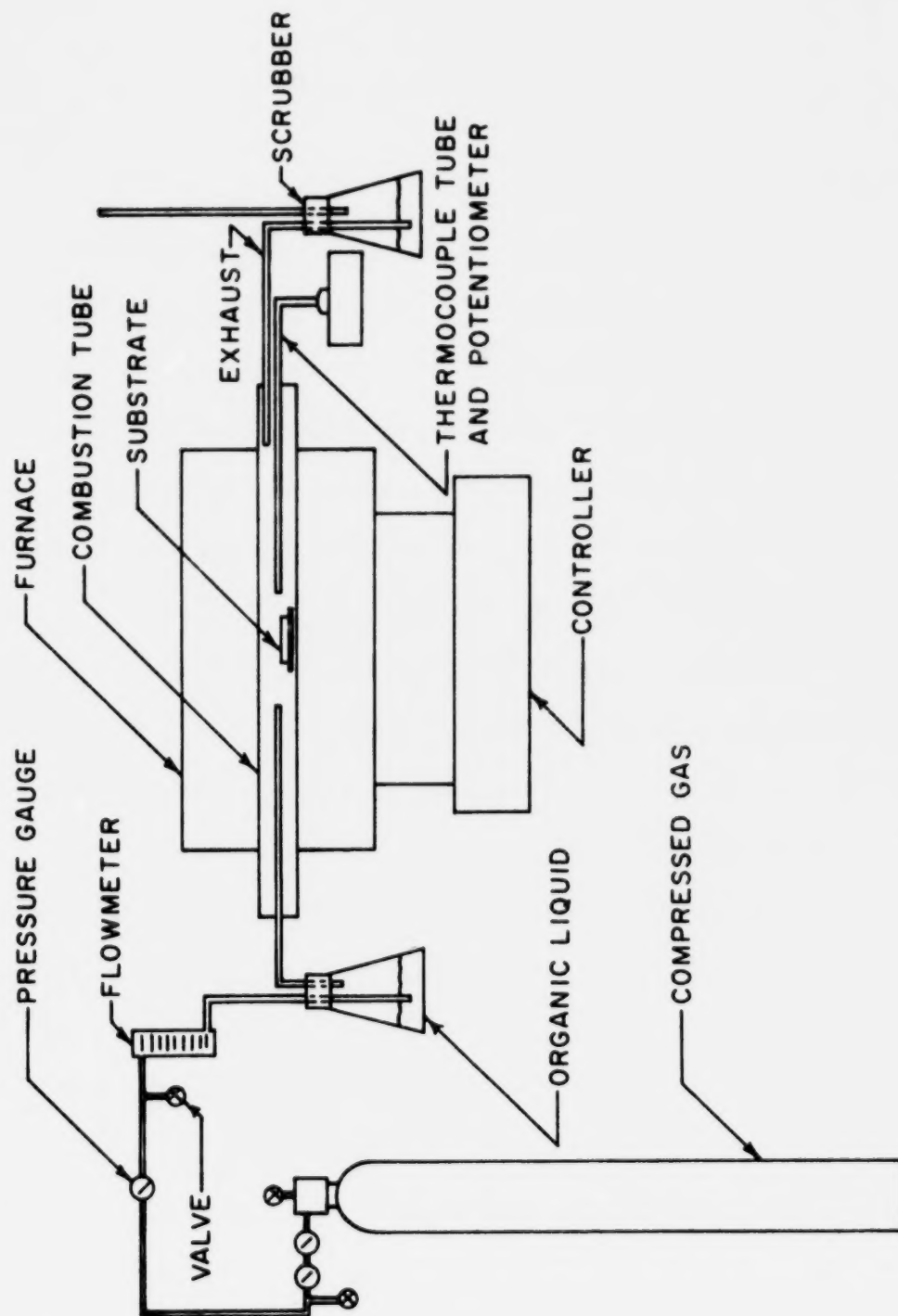


Figure 1. Schematic of the chemical vapor deposition apparatus

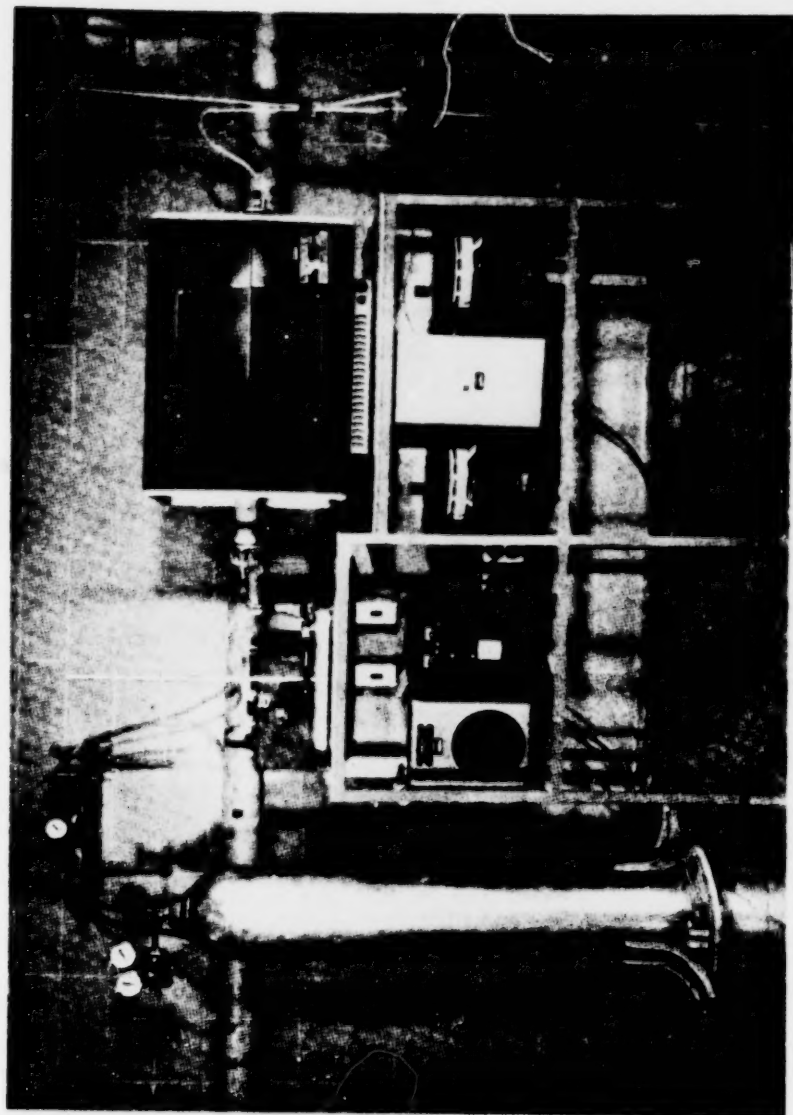


Figure 2. Photograph of the chemical vapor deposition apparatus

30 A review of other designs (11) suggested that the cross-sectional dimensions of the chamber should be as small as practically possible for improved control effects. This consideration is thermodynamically related to gas mixing uniformity and heat transfer effects within the tube (29). It was recognized at the outset of this investigation that two primary control parameters would be temperature uniformity of the substrate on all external faces and a uniform supply of the reactant gas and carrier gas mixture to the substrate. A compact reaction chamber with a small internal volume enhances the control of such variables.

The tube was fired with a 230 volt, 3200 watt Lindberg "Hevi-Duty" laboratory combustion furnace. The furnace measured 25 inches along the axial length of the tube. The unit incorporated eight 1/2 inch by 16 inch series connected silicon carbide heating elements which were arranged transverse to the axis of the tube, four above and four below, on four inch horizontal and vertical centers, to form a twelve inch firing zone.

Excellent temperature control of the unit was readily achieved through the use of a Barber Coleman Model 477 Capacitrol electronic indicating controller to drive a Model 621A silicon controlled rectifier for the proportional control of load power. The solid state circuitry of the Model 477 makes it possible to eliminate temperature overshoot and undershoot by properly adjusting the proportional control action and reset features of the instrument.

The control thermocouple was composed of platinum and platinum alloyed with 13 percent rhodium wires. The junction was maintained in contact with the external face of the combustion tube at the center of the firing zone. The final

location of the controlling sensing element was determined after many trial and error experimental runs which consisted of monitoring the response and recovery characteristics of the above control system to arbitrary changes in temperature and gas flow with the thermocouple junction located inside the firing zone of the combustion tube as well as against the outside face.

For the purpose of the above trials, a monitoring thermocouple was connected to a potentiometer with its junction positioned inside the firing zone of the combustion tube. This thermocouple was also subsequently used during actual coating runs to record the substrate temperature.

In general, it was found that the control characteristics for an externally heated system under stable conditions were excellent for both thermocouple locations. However, process lag and cycling were less for the external thermocouple location when an arbitrary process change was introduced. Mullite heat reflectors were placed inside the tube at the ends of the firing zone to help balance the temperature profile, and with this arrangement, it was possible to maintain plus or minus 2 degrees Fahrenheit ($^{\circ}$ F) at a given spot and plus or minus 15 $^{\circ}$ F at different locations within the firing chamber under stabilized conditions. A schematic representation of the control circuit is shown in Figure 3.

This system as described will operate successfully to 2700 $^{\circ}$ F. However, longer life of the heating elements and thermocouple wires is expected if the temperature does not exceed 2500 $^{\circ}$ F. The unit is readily responsive to input power changes. Heating and cooling rates above 350 $^{\circ}$ F per hour are considered deleterious to extended component life.

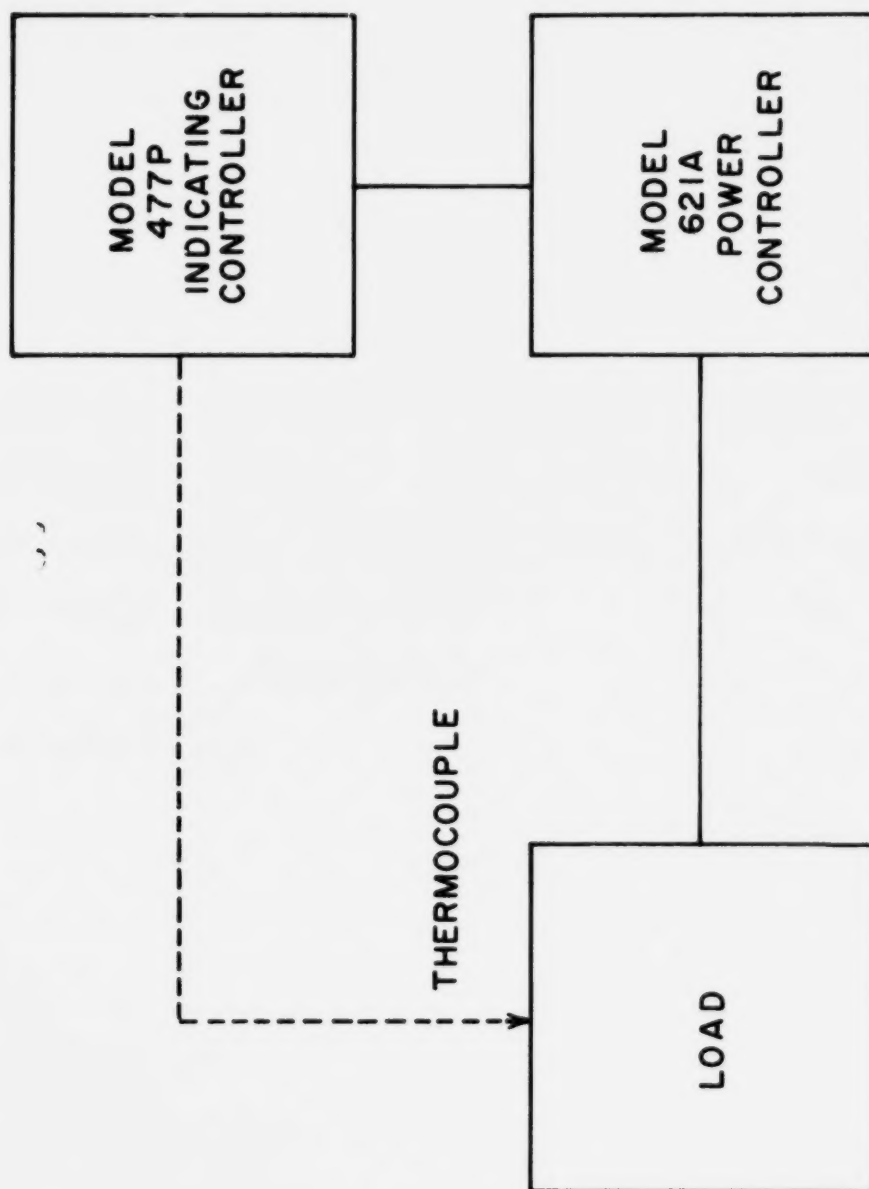


Figure 3. Schematic of the temperature control circuit

Control of the plating vapor concentration in the carrier gas stream over a range of flow rates is important in chemical vapor deposition processes, for such variables partially govern deposit thickness, uniformity, orientation, and purity. For the purposes of this investigation, cylinders of prepurified grade compressed gases were purchased from Matheson Company to serve as the transport vehicle. These gases were pressure regulated on Matheson equipment in two stages to yield a resultant gas force which could be controlled in integral units of water pressure up to 35 inches. This controlled pressure was fed into the system through a flowmeter calibrated to read between 0-10 cubic feet of air per hour (cfh) in increments of 0.25 cfh up to 2 cfh and in increments of 1.0 cfh at higher flow rates. A calibration chart supplied by the vendor allowed different gases to be used with the same flowmeter by applying correction factors to the settings used. The resultant system yielded a highly reproducible, control-sensitive gas supply to the vaporizer.

The liquid plating agents used in this study were vaporized into the carrier gas from a simple 125 milliliter (ml) Pyrex flask. The flask was sealed at the top with a rubber stopper containing two sections of 1/4 inch Pyrex tubing, one to allow for the entrance of the carrier gas and the other for the exit of the resultant gas mixture. A constant temperature water bath was utilized to elevate the vapor pressure of the liquid for those runs that required a higher concentration of plating vapor in the gas stream mixture entering the reaction chamber. Higher temperatures (between 200°F - 500°F) were achieved by using an electrical blanket around the flask, connected through an autotransformer for temperature regulation. The liquid

temperature inside the vaporizer was read with a mercury thermometer, vertically suspended by the rubber stopper at the top of the flask.

The carrier gas was admitted to the vaporizer by bubbling through the liquid, or alternately, by simply passing it over the liquid surface. The type procedure used was found to influence the evaporation rate significantly. In the first case, the carrier gas becomes saturated with plating vapor, whereas in the second case saturation does not necessarily occur. Thus, the bubble-type vaporizer was found to give a constant concentration of plating vapor in the carrier gas over a range of flow rates whereas the non-bubbling type was largely uninfluenced by flow rate except at higher flows and at temperatures near the boiling point of the liquid. Figure 4 depicts the relationship for tetraisopropyl titanate, one of the plating compounds used.

Both methods generally worked satisfactorily for the range of conditions used in this study. However, high vaporization temperatures and high flow rates leading to excessive plating vapor saturation in the gas stream oftentimes resulted in spray formation or misting conditions and subsequent coating defects on the substrate with either method. This situation was partially remedied by wrapping the downstream surfaces of the vaporizer and gas lines with electrical heating tape and packing the interior of the flask with loosely fitting binder free glass cloth to lessen the possibility of the vapor condensing and subsequently reevaporating on downstream surfaces. Such measures however, were only marginally successful and as a result it was concluded that more sophisticated vaporizer design concepts would be required

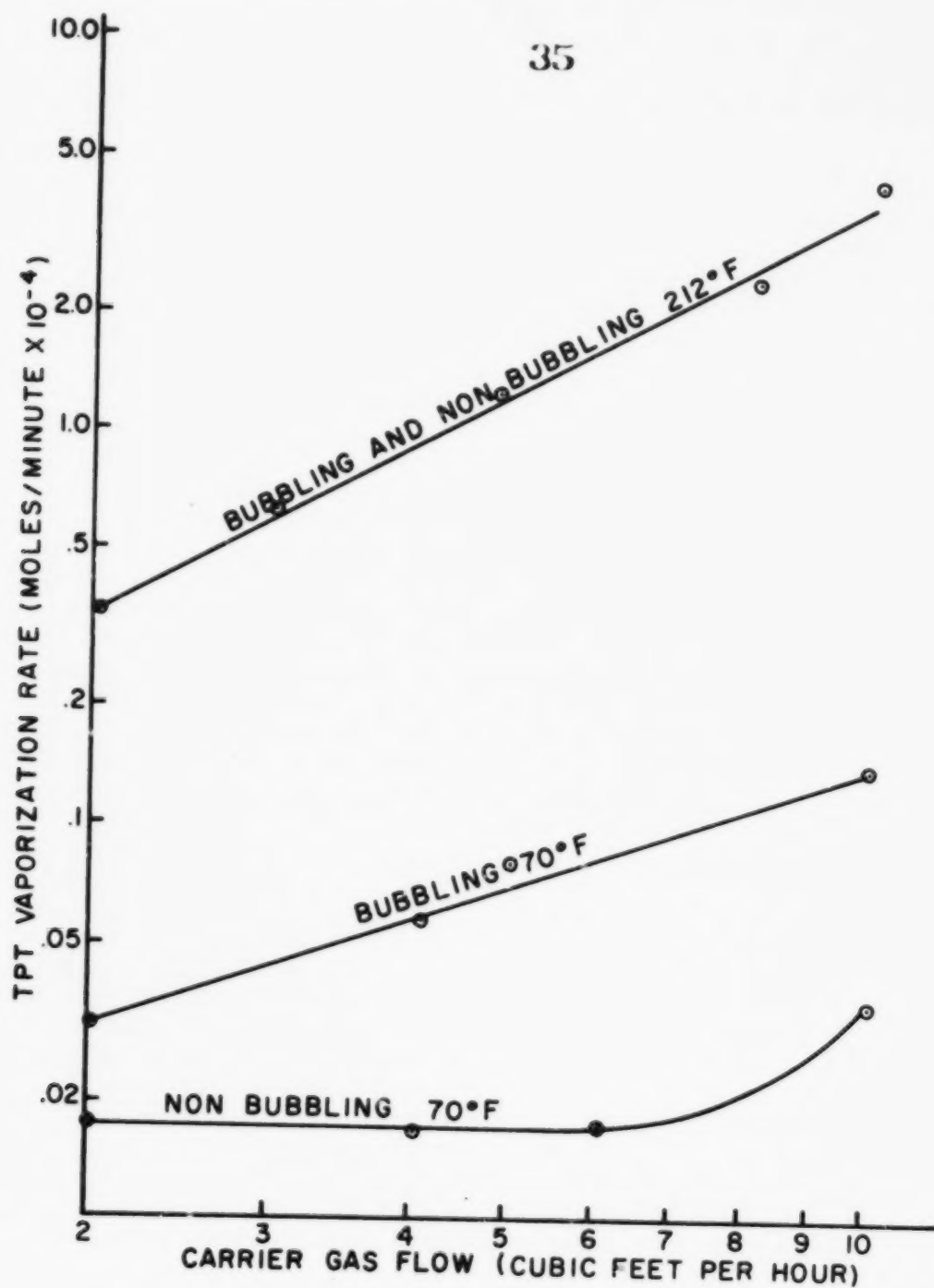


Figure 4. Evaporation rates of tetraisopropyl titanate under bubbling and non-bubbling conditions at different temperatures and carrier gas flow rates

under such conditions. Li (30) and Powell (11) have reviewed some advanced design concepts used in this field.

The vaporizer equipment described thus allowed a given plating compound to be vaporized at a given rate and mixed under controlled conditions with a selected carrier gas. The ability to regulate the concentration of the plating vapor in the resultant gas stream is highly important, as previously mentioned. Appendix 1 contains a sample calculation illustrating the method used to derive plating vapor concentration in the gas stream under a given set of conditions.

After mixing, the effluent gas stream exited the vaporizer by forced convection and passed into a 1/4 inch stainless steel tube leading into the interior of the reaction chamber via an O-ring compression seal mounted on the entrance door. The stainless steel tube was water cooled along its length by a copper coil. The entrance and exit water leads of the coil were also extended through O-ring seals and connected to a nearby water source and drain system. The purpose of the water cooling was to protect the various vapor species from premature decomposition, primarily at higher temperatures and lower flow rates. In many cases, water cooling was not required, and a 1/4 inch Pyrex glass inlet tube was substituted under those conditions to promote cleanliness and lessen the possibility of side reactions. The length of the inlet tube was sufficiently long to allow its terminal end inside the reaction chamber to be pre-adjusted laterally with respect to the substrate position in the firing zone. This arrangement allowed a range of distances between the gas outlet and the substrate to be selected for orientational studies.

After reaction at the substrate, the spent gases were exited through the rear end of the sealed combustion tube, bubbled through 1/2 inch of water level in a 1000 ml Pyrex flask and exhausted through a fume hood collection system erected over the deposition apparatus.

B. Other Design Considerations

As an adjunct to the method of vaporization described above, a method of vaporizing solid materials or liquids with very low vapor pressures was derived. This procedure involved the use of higher temperatures (500°F - 1800°F) supplied by a 120 volt, 1650 watt nichrome wire-wound combustion tube furnace located upstream from the deposition furnace previously described and supplied with a common mullite tube 57 inches in length extending through both furnaces. The smaller furnace was independently controlled with a 120 volt General Radio auto-transformer supplying power to the system as dictated by a Barber Coleman Model 472 Capacitrol indicating time proportioning controller. A chromel-alumel thermocouple vertically located in contact with the external surface of the combustion tube at the center of the 12 inch firing zone served as the sensing element.

For this system, evaporation was carried out inside a 1 inch by 1 inch mullite crucible which contained the substance to be evaporated. The crucible was placed into the center of the firing zone, and a carrier gas passed over its surface. The actual vaporization temperature was read with a chromel-alumel thermocouple located 1/2 inch from the evaporating surface.

Intimate mixing of the gaseous species was difficult to attain, and the method was generally unsatisfactory. However, the system has merit for high

temperatures and should qualify as a satisfactory method if procedures to better direct the gas flow for improved mixing effects are installed. The external arrangement of the complete system is shown in Figure 5.

Efforts to meter liquids dropwise into the gas tight chamber for evaporation proved fruitless. A titrimeter charged with the plating substance was installed above the evaporation furnace and the liquid head produced drops of liquid which entered the chamber by gravity, being collected in a crucible under the influence of controlled heat as described in the preceding paragraphs. The rate of metering did not lend itself to close control by this method since the head pressure of the titrimeter constantly changed. No coatings of value were obtained in this way.

C. Input Material Considerations

The compressed gases used in this study were prepared by Matheson Company. Nitrogen was the primary gas employed, with argon and helium used to a lesser extent. As in all chemical vapor deposition processes, the relative purity level of the carrier gases largely influences coating characterizations and reaction kinetics. The presence of water vapor in these gases was considered especially deleterious because of the pronounced tendency of tetraisopropyl titanate to hydrolyze. As can be seen by a comparison of the molecular weights, 284.2 for tetraisopropyl titanate and 18.0 for water, only a small amount of water is required to reduce a relatively large amount of the plating compound. All compressed gases used were prepurified grade or higher with a purity level of greater than 99.99 percent.

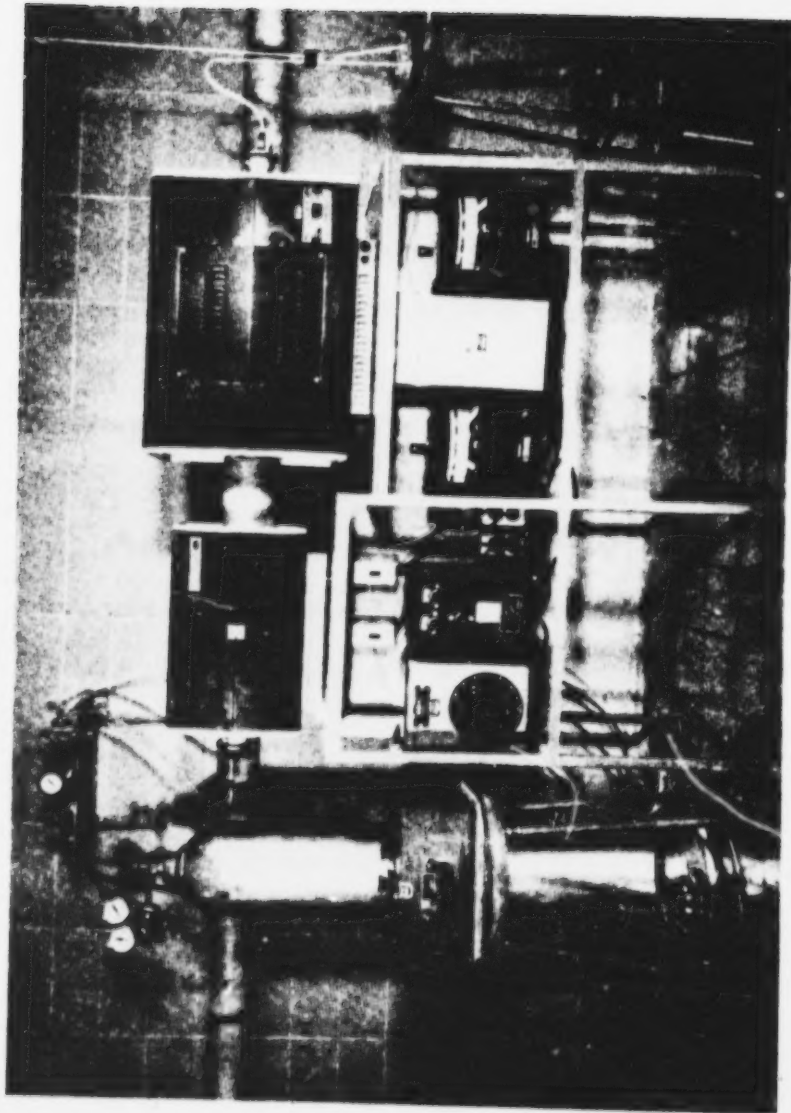
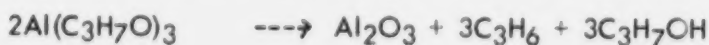
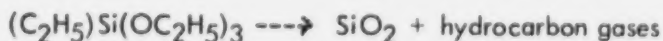
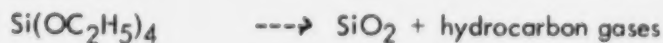


Figure 5. Photograph of dual furnace assembly

The plating compounds used in this study were selected for their ability to yield controlled coatings of desired composition through the medium of chemical vapor deposition. The physical mechanism consists of causing the vaporized plating compound to decompose or pyrolyze at the heated substrate, leaving the nonvolatile components of the compound behind as a chemically bonded coating. Obviously, a coating compound must possess certain characteristics to enable it to be processed in this way. Ideally, it should be a liquid at room temperature with a sufficiently high vapor pressure to obviate the necessity for elevated vaporizer temperatures. Its purity content must be high to minimize the possibility of undesirable contaminants collecting on the substrate and also to prevent the possibility of side reactions neutralizing the plating vapor. Lastly, the source material must be chemically stable even though it is volatile, that is, it must not prematurely decompose, and it should contain only one nonvolatile component. Two organometallic compounds which readily fit these criteria were selected for this investigation. They are tetraisopropyl titanate, $\text{Ti}(\text{C}_3\text{H}_7\text{O})_4$, known as TPT, and ethyl orthosilicate, $\text{Si}(\text{OC}_2\text{H}_5)_4$, known as ETOS. In addition, several runs were made using aluminum isopropoxide, $\text{Al}(\text{C}_3\text{H}_7\text{O})_3$, and ethyltriethoxysilane, $(\text{C}_2\text{H}_5)\text{Si}(\text{OC}_2\text{H}_5)_3$. These materials are all relatively stable liquids with boiling points ranging from 322°F to 478°F . All of these materials yield oxide coatings with the associated metallic cation. Their proposed reaction mechanisms are listed below, in the form of chemical equations.



The purity levels of the plating compounds used were the highest obtainable for stock items from the major chemical supply houses. Generally, this is specified to be greater than 90.0 percent pure. The writer believes that future work in this field should incorporate even higher purity levels if possible to further preclude the possibility of side reactions and impurity deposits. The chemical complexity of these materials requires that they be stored under cool, dry conditions. No evidence of deterioration with time was noticed. Table I may be consulted for chemical information pertaining to the plating compounds.

Glass microscope slides were employed in this study to serve as substrates for all process evaluations. The 1 inch by 1 3/4 inch microslides were composed of Pyrex glass manufactured by W.H. Curtin and Company. These slides were carefully individually washed with warm, soapy water, rinsed, and dried prior to use.

The soluble glass compositions were produced as 1 1/4 inch by 1/4 inch discs. Raw materials consisted of commercial grade sodium carbonate and silicon dioxide weighed and mixed in the proper proportions to yield the desired oxide ratio after melting. The range of compositions studied varied between 43-57 weight percent SiO_2 . Powders were intimately mixed with a V-blender mixer, poured into a mullite crucible and fired to 2500° F. The resultant fused mixture was removed from the furnace after 30 minutes and with the aid of hand tongs was poured into a steel die and pressed into the desired shape. The pressed pellet was rapidly removed from the die and transported to an annealing furnace at 800° F. After stabilization at that temperature for thirty minutes the furnace was deenergized and slowly cooled.

TABLE I

CHEMICAL PROPERTIES OF PLATING COMPOUNDS

MATERIAL (REFERENCE)	FORMULA	MOLECULAR WEIGHT	SPECIFIC GRAVITY	MELTING POINT, °F	BOILING POINT, °F AT A VAPOR PRESSURE OF 60 mm. 400 mm. 760 mm.	
Tetraisopropyl titanate (25)	$\text{Ti}(\text{C}_3\text{H}_7\text{O})_4^*$	284.2	0.955	68	300	410 450
Ethyl orthosilicate (37)	$\text{Si}(\text{OC}_2\text{H}_5)_4^{**}$	208.3	0.935	-121	---	--- 333
Ethyltriethoxysilane (37)	$(\text{C}_2\text{H}_5)_3\text{Si}(\text{OC}_2\text{H}_5)$	192.3	0.889	--	188	282 322
Aluminum isopropoxide (38)	$\text{Al}(\text{C}_2\text{H}_7\text{O})_3^*$	204.3	1.058	223	---	--- 478

*Supplied by K & K Laboratories, Inc.

**Supplied by Fisher Scientific Company

The resultant stress-free product was subsequently removed from the furnace and ground and lapped on conventional metallographic processing equipment using 80, 240, 400, and 600 grit silicon carbide particles. Mechanical polishing was accomplished with 1 micron alumina by Linde. The finished discs were visually inspected at 80x under vertical illumination. Samples exhibiting scratches, pits, or other defects were repolished. The finished product was then stored in a desiccator prior to use.

D. Deposition Techniques

The reaction chamber was charged with glass substrates at room temperature to prevent stress cracking the samples. Immediately after sealing the system, a 1.0 cfh flow of nitrogen sweeping gas was initiated to purge the system. After a five minute purge, the furnace power was turned on. When the substrate temperature reached the specified value as read on the monitoring thermocouple located 1/2 inch away from its surface, the compressed gas flow was adjusted to a specified level and rerouted through the plating compound vaporizer, thus introducing a reactant gas mixture into the deposition zone. The gas mixture was allowed to flow through the furnace for a specified length of time determined by the thickness of the coating required. The furnace was then turned off and purging was resumed until room temperature was reached and the sample removed.

Two methods of holding the substrates in the deposition chamber were devised. Those substrates subjected to the upper temperature limits for glass were simply laid on one face onto a 2 inch by 6 inch sheet of corrugated alumina. The alumina holder tended to protect the substrate from a tendency to slump at the higher

temperatures. The major drawback to this method was that it required an additional coating cycle for the other side of the substrate.

Lower temperature coating operations were alternately carried out by suspending the substrate vertically with the front face perpendicular to the gas stream. The substrate was held by the hooked ends of a short length of wire which was spirally wrapped in the middle portion around the outside of the monitoring thermocouple insulator tubing for anchoring purposes. In this manner, minimum surface contact with the substrate was maintained. This mode of orientation allowed some coating to be deposited on the back side of the sample at higher gas flow rates. In addition, this method of suspension allowed the substrate to be rotated during the coating operation, thereby improving the overall coating uniformity to a high degree. Rotation of the sample during a run was accomplished by exerting a torque on the monitoring thermocouple insulator tubing extending through the exit end of the reaction chamber. The insulator tubing was linked to the heat reflector and substrate, and twisting it through a given angle transformed the same rotation to these components inside the chamber. The arrangement of the two substrate positions is shown schematically in Figure 6.

It was found that several successive runs tended to produce such contamination products as non-adherent white powder particles on the interior surfaces of the chamber. These were analyzed and found to be either TiO_2 or SiO_2 , depending upon the plating material used. Black soot (presumably carbon) and oily spots (partially polymerized silane from ethyltriethoxysilane) were also observed. These substances were easily removed with a warm detergent solution, with the exception

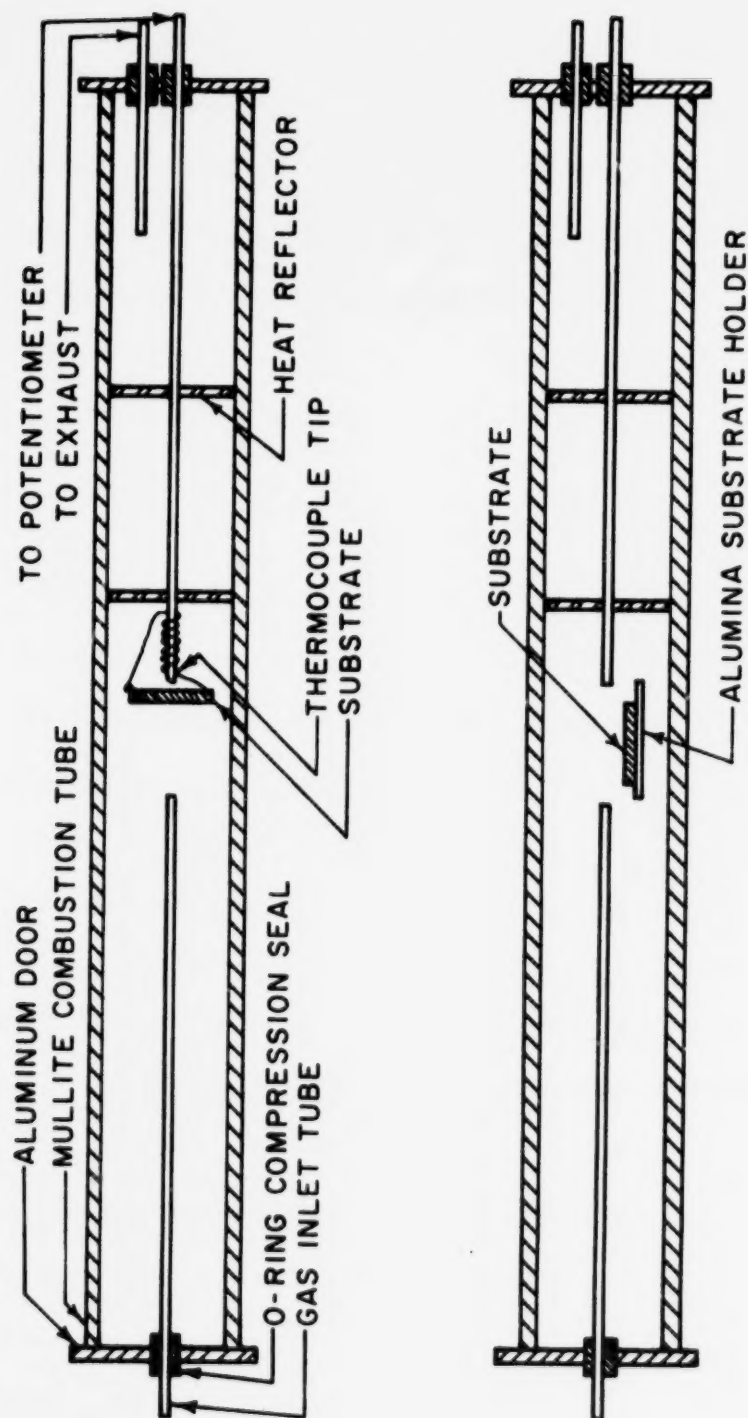


Figure 6. Schematic of the substrate positions used. The top view shows the substrate in a vertical position. The bottom view shows the substrate in a horizontal position.

of the carbon, which was removed only under high temperature oxidizing conditions. Silica glass was also found inside the tube after a series of runs. It was removed periodically by scrubbing with a weak solution of hydrofluoric acid. These contaminants did not noticeably alter any results, although their effect on coating defects was not definitely established. Jordan (31) reported no deleterious effect from silica contamination using a similar process for coating semiconductors, where purity level is critical.

E. Analytical Procedures

1. Microscopy

The coatings obtained were viewed under a vertically illuminated Leitz Panphot metallographic microscope, and photographic work was accomplished on this equipment with the aid of a Nikon photomicrographic attachment coupled to a 35 millimeter (mm) Leica camera. The photomicrographs yielded information primarily related to the defect structure and orientation of the deposits.

2. Phase Analysis

Chemical phase analyses of the TiO_2 coatings were determined with the aid of X-Ray diffractometry and spectroscopy, using Norelco instrumentation. The structure of the deposit was determined by observing the presence or absence of diffraction lines for a given material, using copper K-alpha radiation, 30 kilovolts and 10 milliamps. TiO_2 deposits which failed to diffract X-Rays were declared to be amorphous; those deposits which exhibited characteristic diffraction peaks were crystalline.

Crystalline SiO_2 was determined by the same method outlined previously. The silica glass was detected by X-Ray diffraction and infra-red spectroscopy. The broad, diffuse pattern revealed by the diffractometer was not considered to be very definitive, so the spectroscopy technique was primarily relied upon. A Perkin-Elmer 621 Grating Infrared Spectrophotometer was utilized for the production of these data. It was necessary to use a substrate which was transparent to infrared energy, so glass was replaced by a 10 mil wafer of semiconductor grade silicon, which served as the base for the deposited coating.

3. Coating Thickness and Uniformity

The TiO_2 coatings provided an additional dimension to the analytical techniques used because they were found to produce optical interference colors when deposited on glass. The presence of these colors is related to the differential refractive index between the substrate and the coating, as well as the coating thickness. An excellent review of the subject is provided by A. Vasicek (32).

Generally, the color fringes may be interpreted in the same way one reads a topographic map, except in this case the differential thickness between bands of the same color equals one-half of the wavelength of light transmitted through the film producing that color. Figure 7 illustrates the concept. The target effect in photograph (A) resulted from the plating vapor contacting the substrate in a concentrated stream rather than diffusing out to produce a more uniform color, as seen in (B). Both of these samples contained roughly the same amount of coating by weight. However, the coating on the left varied progressively in thickness across its surface,

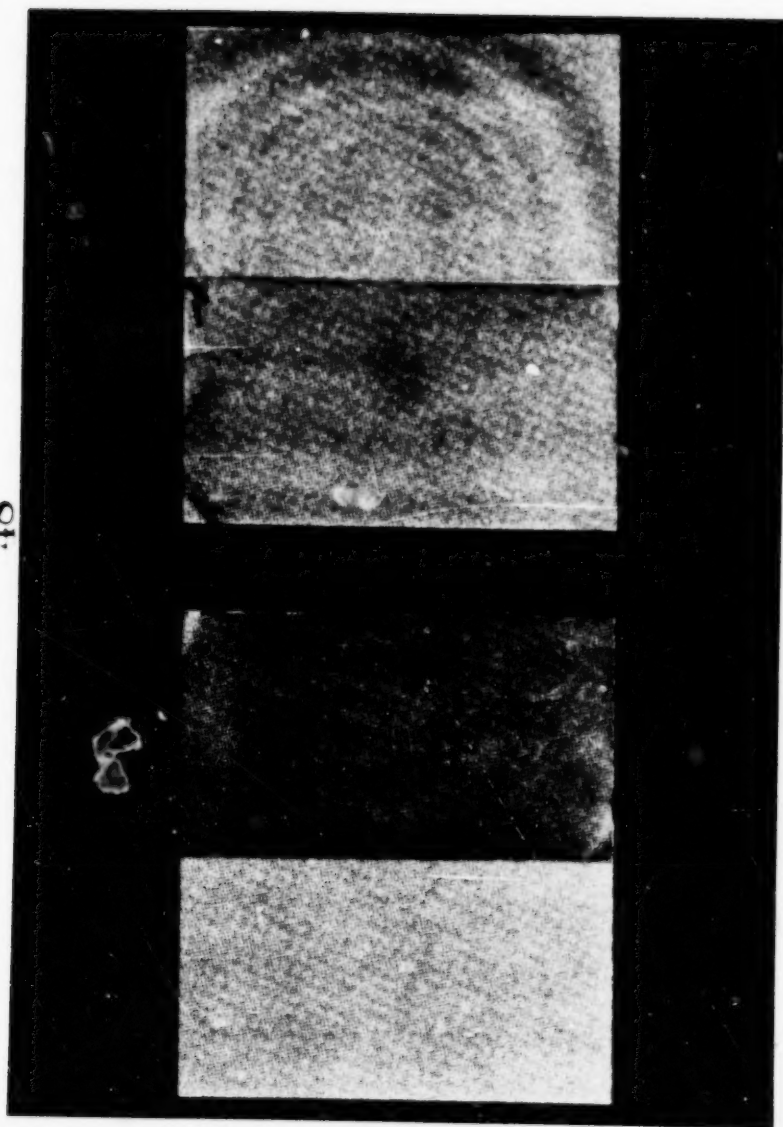


Figure 7. Analysis of TiO_2 film thickness and uniformity shown by interference colors. All films were derived by bubbling nitrogen gas through TPT at 2120 F. Exhibit (A): Carrier gas flow 4 cfh; deposition temperature 5750 F; substrate orientation 4 inches; time 15 minutes. Exhibit (B): Carrier gas flow 10 cfh; deposition temperature 7650 F; substrate orientation 10 inches; time 30 minutes. Exhibit (C): Carrier gas flow 10 cfh; deposition temperature 7650 F; substrate orientation 10 inches; time 5 minutes. Exhibit (D): blank sample.

whereas (B) was coated relatively evenly, resulting in an average thickness of approximately 3000 Å. Photograph (C) depicts an extremely thin, uniform coating, approximately 500 Å in thickness, which may be contrasted with the uncoated sample (D). Whereas the thin films (less than 1000 Å) were highly reflective, as a silvered mirror, if crystalline, or merely tinted if amorphous, the thick films (over 50,000 Å) were opaque and reflected little light.

Thus, the TiO_2 films were easily interpreted visually for uniformity and thickness. Such was not the case for SiO_2 films which yielded no colors because of a close similarity of refractive indices between the coating and the substrate.

Alternately, film thickness was measured by weighing the specimen before and after coating on a Mettler grammatic balance. The weight gain represented the amount of coating deposited on the substrate, accurate to 0.0001 grams. The average coating thickness was computed from the following formula:

$$t = \frac{w}{(d)(A)(10^{-8})}$$

where

t = coating thickness in Angstrom units

w = weight gain of substrate in grams

d = density of coating in grams per cubic centimeter

A = area of coating surface in square centimeters

Use of the foregoing relationship yielded an average thickness for all exposed surfaces coming in contact with the plating vapor. Thus, to be used with validity, steps were taken to insure that all surfaces of the substrate received equal coating

treatment by rotating the sample and reversing its orientation as required, or alternatively to mask out all surfaces except the one being coated. This last procedure was accomplished on microslides by pressing two faces together as in a stacking sequence, coating the composite, and separating the two microslides after coating to reveal one uncoated surface for each slide, as well as one coated surface. Of course, the weighing procedure is unable to distinguish between a diffusion coating and an overlay coating. For this reason, its use is restricted to lower temperature coating operations (below 1500° F).

Table I lists the refractive indices and densities of all coatings and substrates used in this investigation.

4. Coating Efficiency

Chemical vapor deposition processes inherently produce low deposition efficiencies which are consequently a major cost control factor, especially since the plating substances involved are oftentimes very expensive (13). Therefore, the efficiencies yielded by this process were carefully studied. The coating efficiency for a given run was derived by comparing the weight gain of the substrate during a coating run to the weight loss of the coating material in the substance being vaporized and expressing the result as a percentage. The amount of plating vapor in the substance being vaporized is derived from a balanced chemical equation of the reaction. Gravimetric measurements were obtained on the Mettler balance described previously. The method of computing coating efficiency is illustrated in Appendix II.

TABLE II

OPTICAL PROPERTIES OF COATINGS AND SUBSTRATES

	INDEX OF REFRACTION	DENSITY, g/cm ³
I. Coatings		
A. SiO ₂ glass	1.43 (22)	2.20 (22)
B. TiO ₂ anatase	2.54 (39)	3.84 (39)
C. TiO ₂ amorphous	----	----
II. Substrates		
A. Pyrex Microslides	1.46 (7)	2.23 (7)
B. 1.0Na ₂ O·1.3SiO ₂	1.51 (7)	2.42 (7)
C. 1.3Na ₂ O·1.0SiO ₂	1.52 (7)	2.43 (7)

5. Coating Stresses

As mentioned earlier, the fact that vapor deposits are applied at elevated temperatures usually leads to residual stresses, primarily caused by thermal expansion coefficient differences between the deposit and the substrate. Powell (33) has pointed out that stress analysis in chemical vapor deposition systems is complex because thermal expansion stresses tend to mask out smaller stresses which may arise from other sources. In addition, elevated coating temperatures sometimes allow stress relief to take place by diffusional and other relaxational processes. The use of glassy materials introduces an additional dimension of complexity into any stress analysis calculation, because their mechanical properties generally present anomalies which are well known (7). The strength properties of glass are largely controlled by surface conditions.

Table III contains the mechanical property constants of the various materials used in this study. They may be used in conjunction with the calculation of residual stresses between a coating and substrate. Appendix III contains an explanation of the procedure used to derive the residual stress.

MECHANICAL PROPERTIES OF COATINGS AND SUBSTRATES

	MODULUS OF ELASTICITY, E, psi	COEFFICIENT OF THERMAL EXPAN- SION, α , /° F	TENSILE STRENGTH, psi
I. Coatings			
A. SiO ₂ Glass	10×10^6 (40)	0.55×10^{-6} (40)	7250 (40)
B. TiO ₂ Amorphous	---	---	---
C. TiO ₂ Anatase	---	---	---
D. TiO ₂ Rutile	41×10^6 (41)	4.9×10^{-6} (41)	7500 (41)
II. Substrates			
A. Pyrex Microslides	9×10^6 (7)	3.2×10^{-6} (7)	8900 (7)
B. 1.0Na ₂ O·1.3SiO ₂	10×10^6 (7)	14.0×10^{-6} (7)	---
C. 1.3Na ₂ O·1.0SiO ₂	10×10^6 (7)	14.0×10^{-6} (7)	---

RESULTS AND DISCUSSION OF RESULTS

A. Effect of Process Variables Upon Reaction Kinetics

The coating process variables associated with a given vapor deposition system are interrelated in a complex manner, and are uniquely dependent upon the geometry of the unit, as well as upon the chemical characteristics of the coating materials and the substrate used. It is therefore important to understand that although the general relationships among the process variables of a given system are valid for all systems, the translation of absolute data from one system to another is not.

For this work, a series of TiO_2 coating runs were made over a range of controlled conditions in order to study the effects of important variables upon deposition rates and coating efficiencies. These variables and their limits of investigation were as follows:

VARIABLE	LIMITS
1. Substrate temperature, ° F	450-1085° F
2. Coating time, minutes	5-75 minutes
3. Carrier gas flow rate, cfh	2-10 cfh
4. Substrate orientation, inches*	2-12 inches
5. Reactant gas concentration in carrier gas (ppm) at a given flow rate	19-2300 ppm

*Substrate orientation may be defined as the lateral distance in inches between the effluent end of the input gas tube and the front face of the substrate.

TiO_2 coatings from tetraisopropyl titanate were selected for this study because of their ease of application to glass substrates over a wide range of conditions. By contrast, SiO_2 coatings from ethyl orthosilicate are energetically feasible only within a narrow range of temperatures immediately below the softening point of the substrate.

1. Substrate Temperature

Figure 8 illustrates the strong influence that the temperature of the substrate exerts over the deposition rate and coating efficiency. A linear relationship was found to exist for the range of conditions investigated. It is especially interesting to observe that for the temperature range shown the efficiency can be increased by a factor of four merely by operating at the upper temperature extreme rather than the lower. It is anticipated that the curve shown would begin to deviate from linearity at higher temperatures with an accompanying decrease in plating efficiency because of premature decomposition of the vapor species inside the reaction chamber.

2. Coating Time at Different Temperatures

Figure 9 depicts the interesting effect exhibited by coating time upon deposition rates at different temperatures. The coating grown at the lower temperature was characterized by an initial period of slow growth, known as an induction period, and a subsequently increased rate of steady-state growth thereafter. This dual growth rate effect was absent in the higher temperature coating which grew at a faster rate, as seen by the slopes of the two curves. The overall coating efficiency for the low temperature coating was severely damaged by the presence of the induction period.

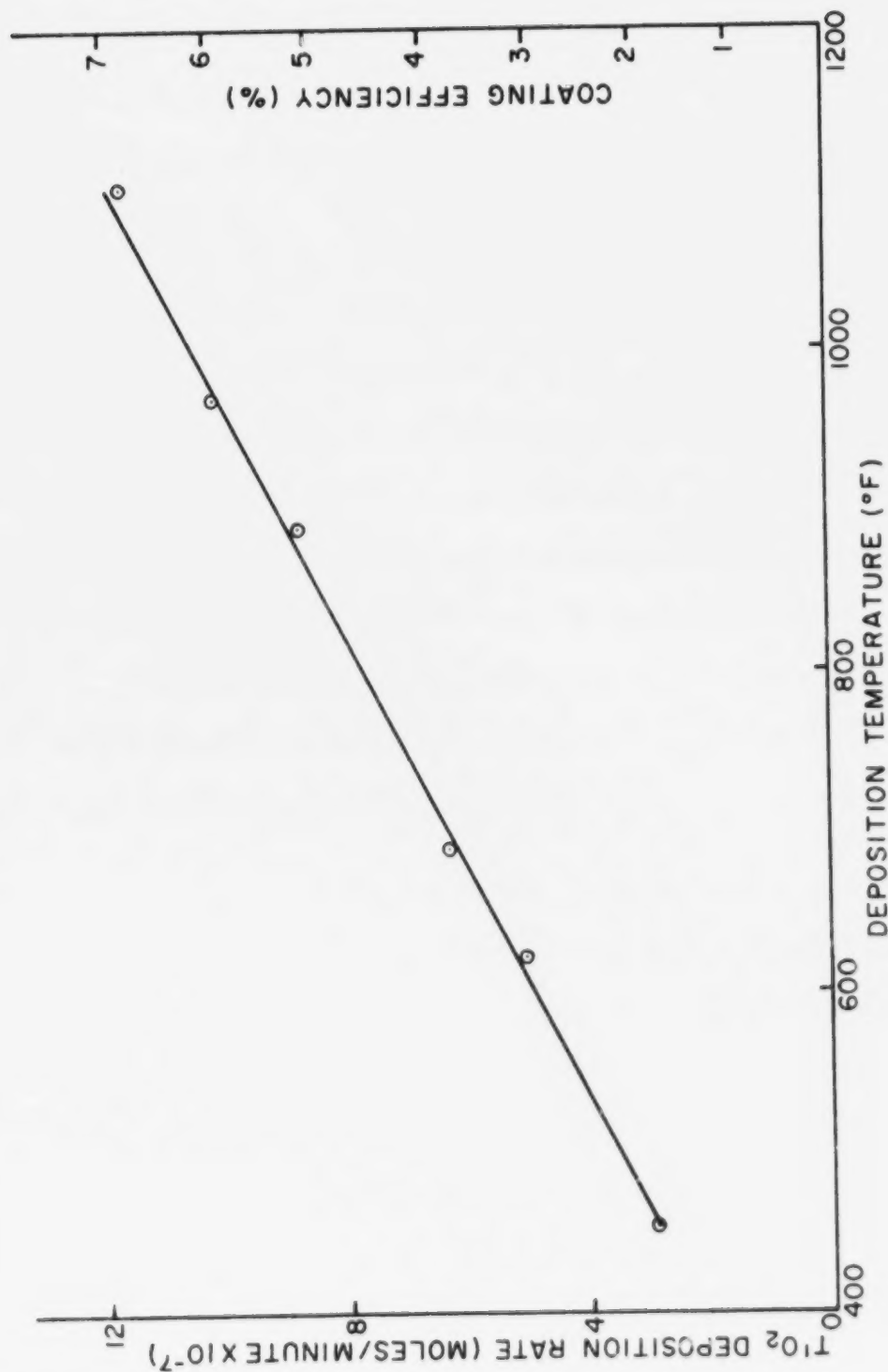


Figure 8. Plot of TiO_2 deposition rates and coating efficiencies at different deposition temperatures. The data was derived by bubbling nitrogen gas through TPT at 10 cfm; vaporization temperature 70°F ; substrate orientation 4 inches; time 60 minutes.

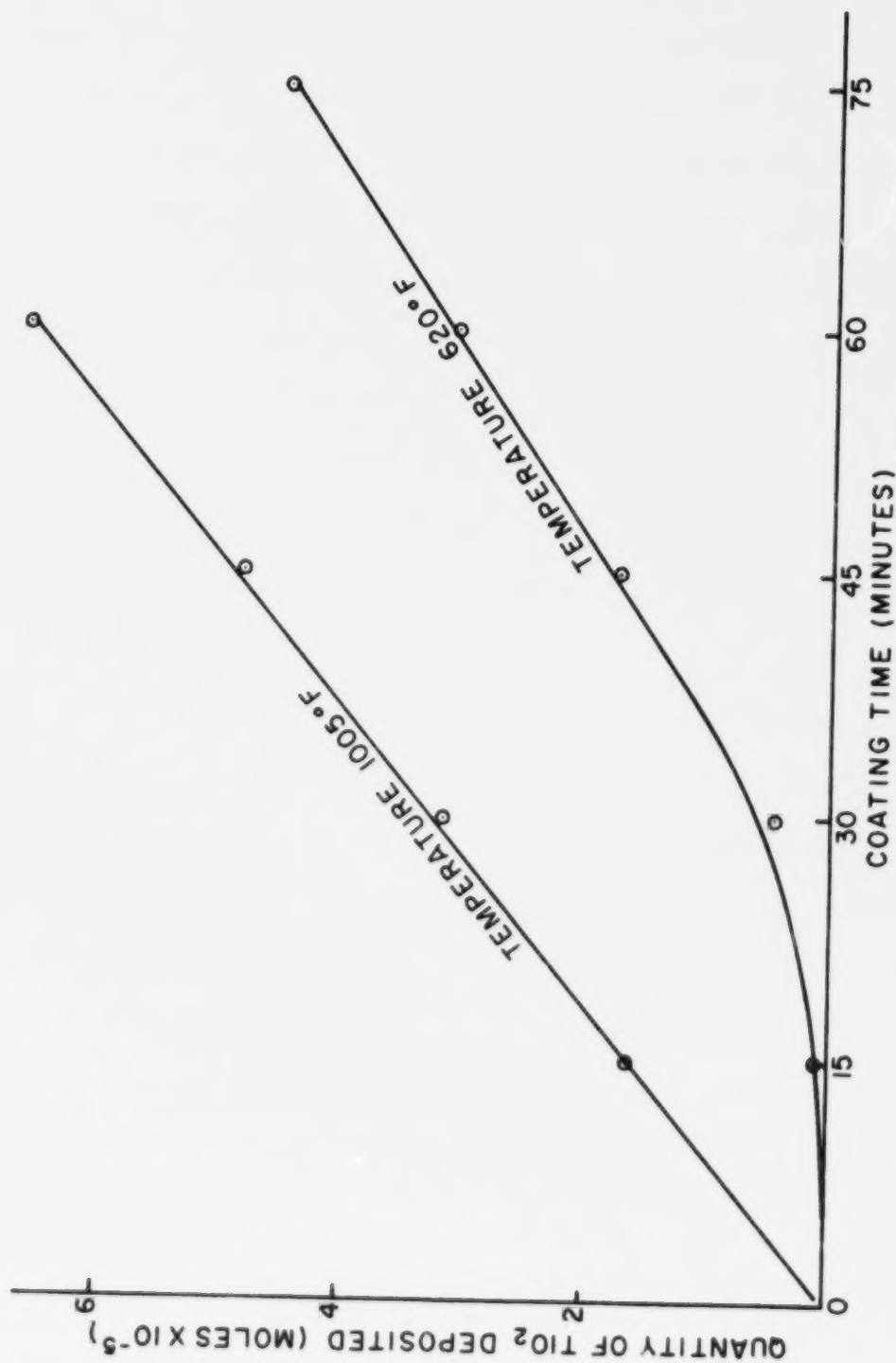


Figure 9. Plot of TiO_2 deposition rates at two different deposition temperatures for varying coating time periods. The data was derived by bubbling nitrogen gas through TPT at 10 cfm; vaporization temperature 70°F ; substrate orientation 4 inches.

3. Carrier Gas Flow Rate and Substrate Orientation

The carrier gas flow rate plays an important role in coating reaction kinetics, as shown by Figure 10. The relationship is especially important when considered as a function of the substrate orientation. The plot shown illustrates the effect of two different flow rates upon the coating efficiency at different substrate orientations. Coating reactions at a given gas flow rate were generally enhanced by decreasing the mean average time of residence of the reactant vapors in the deposition zone prior to contacting the substrate. This of course, was readily accomplished by decreasing the substrate orientation. Curiously, however, this relation did not hold at extremely short distances, presumably because the increased cooling effect of the impinging gases on the substrate was sufficient to retard the reaction.

A change in gas flow promoted marked changes in the reaction rate--substrate orientation profile, as shown. Reaction rates under low gas flow conditions were highly sensitive to the substrate orientation. To illustrate, for the data shown, the coating deposition rate and efficiency at two cfh varied from a maximum at two inches to no reaction at all at six inches, whereas these parameters did not change appreciably in this range at the higher flow rate, although the maximum attainable reaction rate at the higher flow was less than one-half that which could be developed by the lower gas flow condition.

4. Reactant Gas Concentration

TiO₂ coatings were readily obtained over a range of reactant gas concentrations in the carrier gas stream at total flow rates ranging from two to ten cfh.

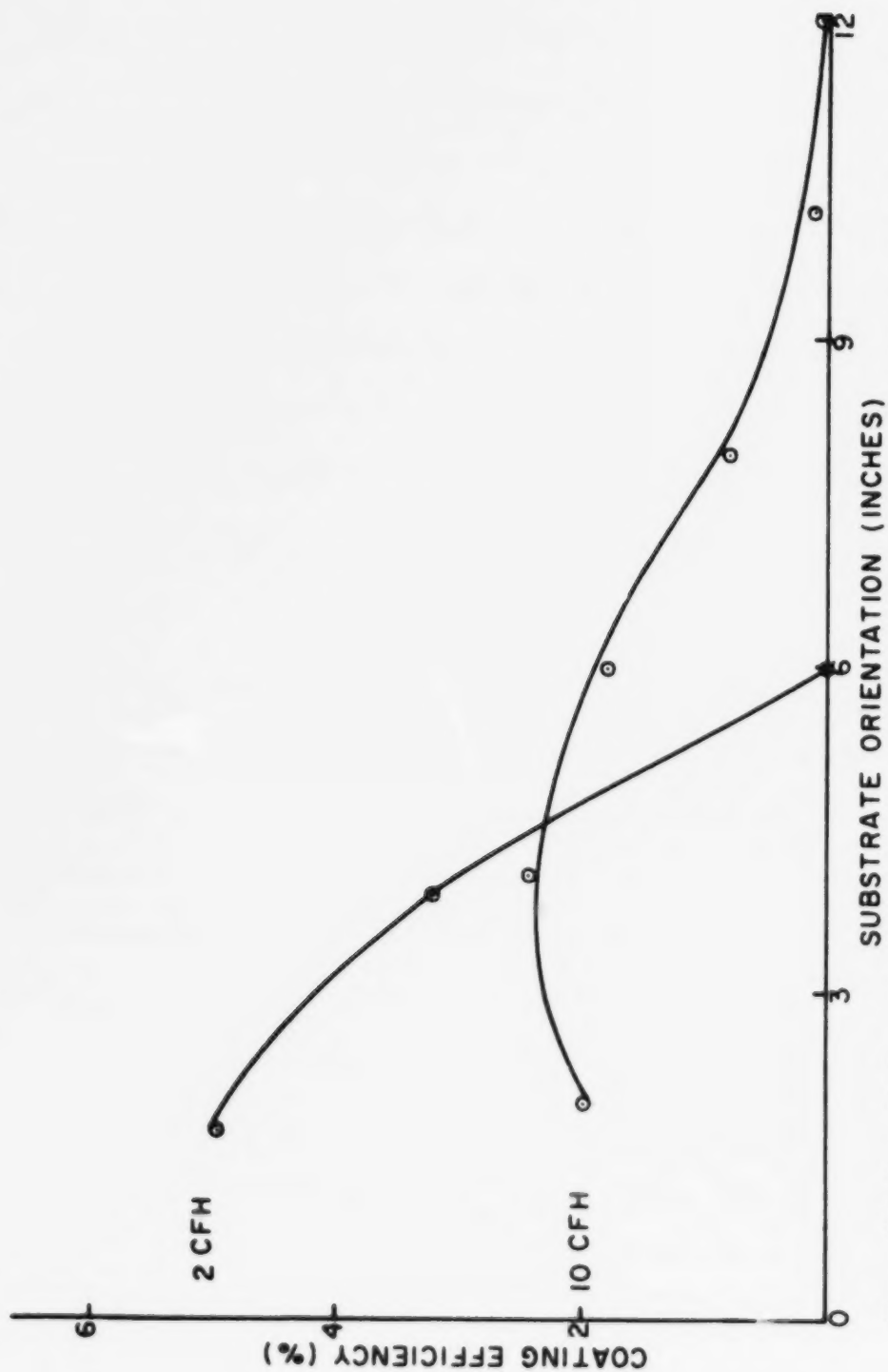


Figure 10. Plot of TiO_2 coating efficiencies at different substrate orientations and carrier gas flow rates. The data was derived by bubbling nitrogen gas through TPT; vaporization temperature 212°F ; deposition temperature 620°F ; time 5 minutes.

The deposition rate was found to vary linearly with concentration at a given total flow rate, as shown by Figure 11. The coating efficiency for these runs was generally the same. The quality of the coatings produced at the different concentrations was significantly affected, however. At high concentrations, the adherence was poor and the coatings examined showed split and cracked areas. These samples were frequently covered with a loosely-adherent brownish colored powder which was found to be a mixture of TiO_2 and carbon. Many of the coatings produced exhibited a dirty cast, indicative of carbon inclusions in the deposit. None of these adverse conditions were found in deposits grown under similar conditions at lower reactant gas concentrations.

B. Coating Stresses

The coating stresses developed by SiO_2 coatings applied to either Pyrex microslides or soluble glass substrates were compressive in nature, and very pronounced, as would generally be expected from an inspection of the physical constants involved in the stress calculation as well as the high deposition temperatures employed. An example of a highly stressed SiO_2 coating is shown in Figure 12. In this case, the coating was applied to a Pyrex microslide at 1220°F . During the initial stages of the cooling cycle sufficient differential stress developed to warp the four corners of the substrate while the glass was plastic enough to flow. Further cooling with the glass in a warped, rigid condition subjected the coating to a combined compressive shear stress which caused it to craze.

Depending upon conditions, several SiO_2 coated soluble glass substrates cracked in tension under the influence of the residual stress developed during the

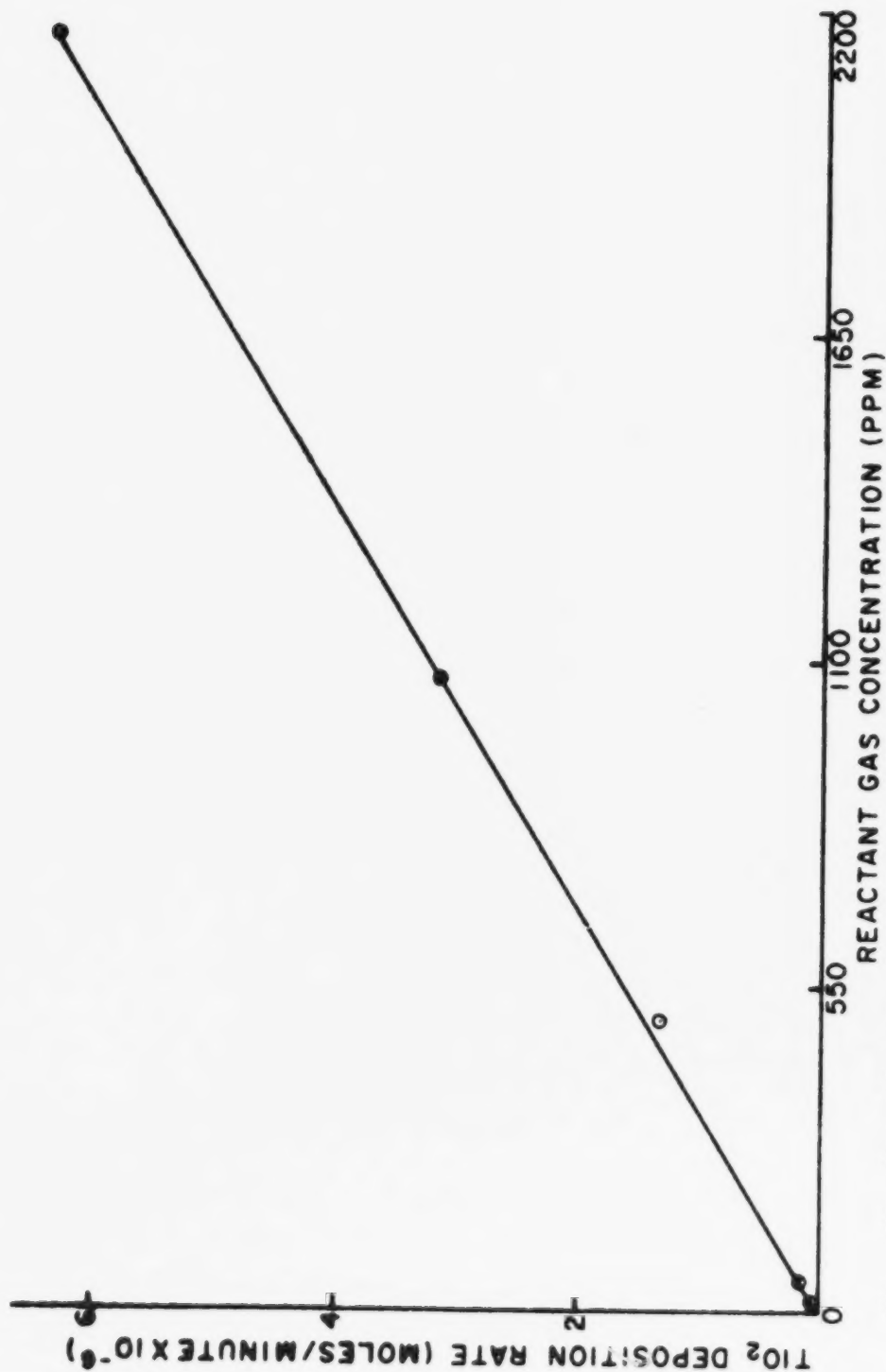


Figure 11. Plot of TiO₂ deposition rates at different reactant vapor concentrations. The data was derived by mixing the carrier gas with TPT under both bubbling and non-bubbling conditions and the vaporization temperatures regulated between 70° F - 212° F; carrier gas flow rate 8 cfm; deposition temperature 780° F; substrate orientation 4 inches; time 15 minutes.

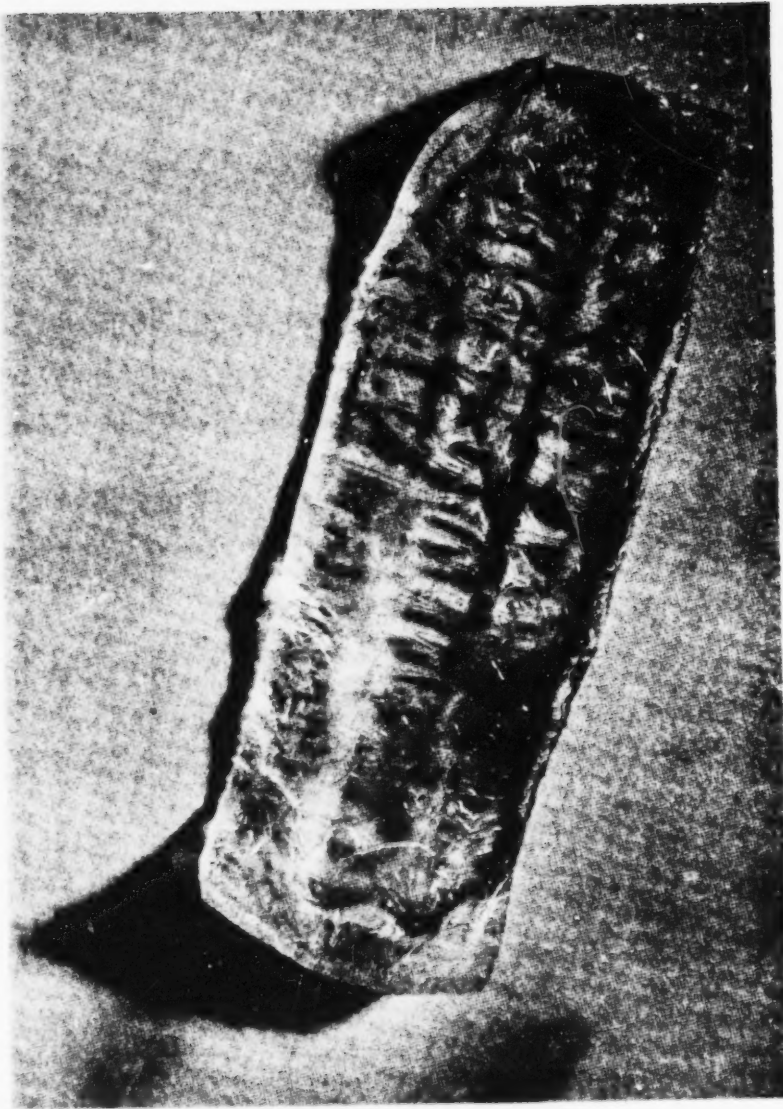


Figure 12. Photograph of high residual stress in SiO_2 deposit. The coating was derived from ethyl orthosilicate vaporized into nitrogen gas at 1 cfm; vaporization temperature 70°F ; deposition temperature 1220°F ; substrate orientation 3 inches; time 14 hours.

cooling cycle, and others were sufficiently weakened to allow manual breakage by application of a torque to the stressed sample.

Despite these obvious drawbacks, satisfactory coatings were developed by resorting to low-temperature slow growth techniques. In this case, temperatures did not exceed 1050°F , and the resultant product demonstrated adequate mechanical properties.

TiO_2 coatings were found to develop smaller compressive stresses on soluble glass substrates, because the temperature of deposition was generally much lower and the thermal expansion coefficients were more closely matched. Coatings applied to borosilicate microslides actually developed a small tensile stress. Yet even under these much improved conditions, TiO_2 coatings could be made to produce a definite crack pattern, provided the coating conditions were not properly controlled. Figure 13 illustrates two TiO_2 coatings produced at 780°F and a reactant gas concentration of 2150 ppm in the gas stream flowing at a rate of eight cfm. In this case, the concentration of the reactant vapor distributed within the carrier gas was very high and non-uniform. In fact, small droplets of tetraisopropyl titanate actually contacted the substrate prior to decomposing, and it is believed that this factor was primarily the reason for the failure of the coating. Figure 13(B) shows the mode of failure to be a tensile stress in the coating.

In general, edges along the substrate surfaces developed stress concentrations, and coating could be made to flake off along these points under relatively low abrasive shear stresses. This was especially noticeable for the thicker films of SiO_2 (over 75,000 Å) and did not appear prevalent on the thinner coated specimens.

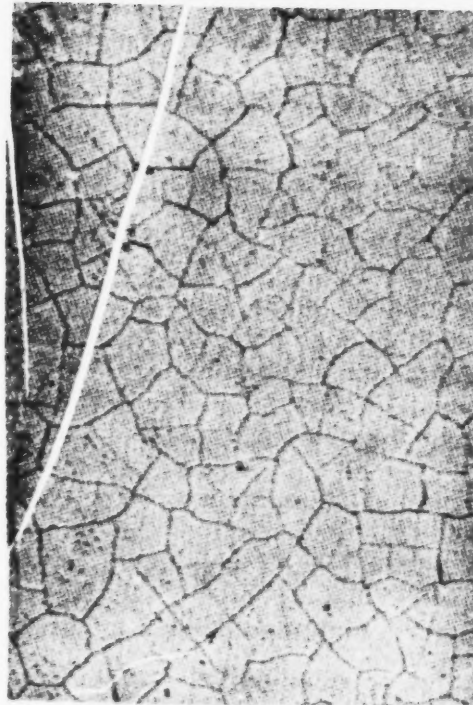


Figure 13. Photomicrographs of residual stresses in a TiO_2 deposit. Exhibit (A): thin coating. Exhibit (B): thick coating. These coatings were derived by bubbling nitrogen gas through TPT at 8 cfm; vaporization temperature 212°F ; deposition temperature 780°F ; substrate orientation 4 inches; time 15 minutes. One inch on photomicrographs equals 88.9 microns.

Coating uniformity was found to depend chiefly upon the ability of the system to deliver a constant supply of plating vapor to all surfaces of the substrate under uniform temperature conditions. Generally, the substrate temperature was well balanced for all conditions investigated, with the design previously described.

A uniform dispersal of the plating vapor to all surfaces of the substrate was more difficult to attain, especially for the TiO_2 coatings. The deposit tended to build up primarily on the front face of the vertically-positioned substrate with a characteristic pattern, most notably the concentric circle effect referred to earlier, which was a direct consequence of the non-turbulent flow characteristics of the system. Geometric limitations precluded the possibility of practically achieving turbulent flow within the tube. As measured by the Reynolds number, N_{Re} , the criteria for turbulent gas flow within the system would have required a cost prohibitive carrier gas flow rate of almost 200 cfh. In addition, the cooling effect from this amount of gas flow would probably have rendered temperature control inside the tube more difficult to attain.

For the above reasons, the control of coating uniformity was achieved in other ways. Periodic rotation of the substrate within the coating chamber during a run was found to even out the deposition pattern of TiO_2 coatings considerably. In addition, the act of increasing the substrate orientational distance relative to the effluent end of the input gas tube while simultaneously increasing the carrier gas flow rate improved the TiO_2 coating uniformity to a high degree by allowing the gases to disperse and more intimately mix prior to contacting the substrate. Although

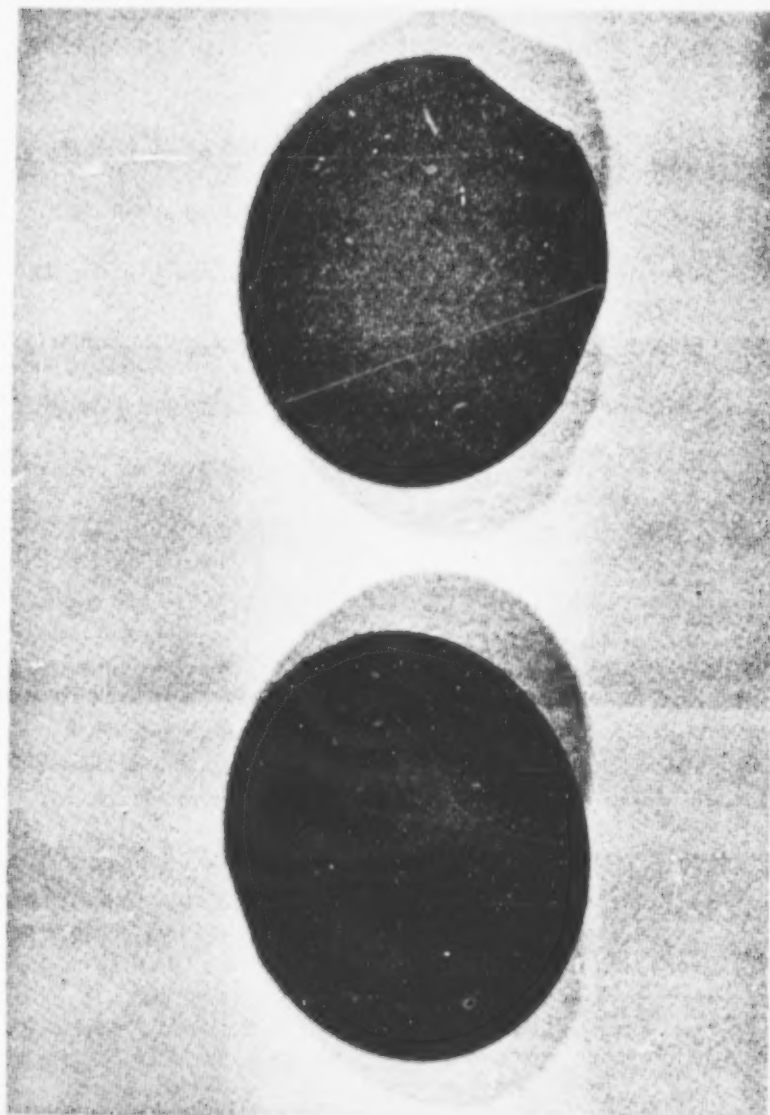
this procedure had a detrimental effect on coating efficiency (see Figure 10) the uniformity for thin coatings was greatly enhanced (see Figure 7).

The influence of generally higher temperatures for the SiO_2 coatings tended to more effectively disperse the plating vapor prior to contacting the substrate, through the medium of thermal energy. As a consequence, relatively uniform SiO_2 overlay coatings were developed without resorting to the physical and mechanical dispersion methods described for TiO_2 . Figure 14 illustrates the deposition pattern for a thick film of SiO_2 deposited onto a thin wafer of semiconductor grade silicon. The coating is approximately 40,000 Å in thickness and is interpreted through the medium of interference colors to be very uniform in the central portions of the wafer with a gradual tapering off in thickness around the edges. Thinner coatings would probably be even more uniform.

D. Substrate Considerations

The important role played by the substrate in vapor deposition operations has been well documented in the literature. In addition to its already discussed influence on residual stresses, the physical and chemical properties of a given substrate are capable of influencing the nucleation kinetics of a given system (34), the structure and properties of the deposit formed (35 and 36) and the bonding strength of the deposit (11).

These important effects are believed to be operative in the system discussed in this paper. Furthermore, the use of soluble silicate substrates for vapor deposited coatings represented the addition of another major variable to be considered. These



(A)

(B)

Figure 14. Photograph of a representative deposition pattern for SiO_2 deposits. Exhibit (A): coated silicon wafer. Exhibit (B): blank sample. The deposit was derived by bubbling nitrogen through ethyl orthosilicate; carrier gas flow rate 2 cfh; vaporization temperature 70°F ; deposition temperature 1350°F ; substrate orientation 3 inches; time 12 hours.

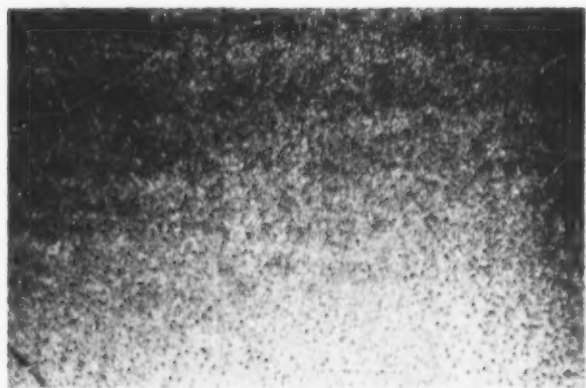
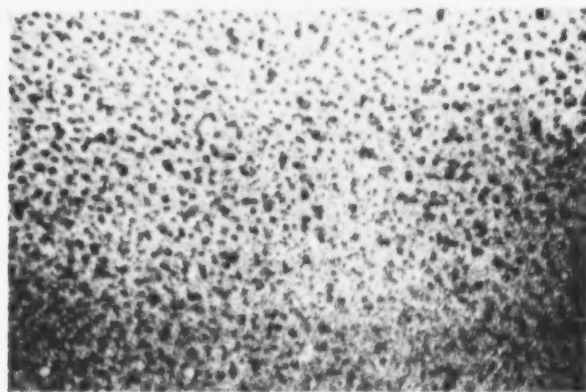
materials, which have a profound affinity for moisture, must be handled and processed under special conditions if controlled coatings are to be obtained on their surfaces. No reports were found of previous vapor deposition work dealing with this class of materials.

One may readily gain an insight into the dynamic solution kinetics of a typical composition used in this study by referring to the sequential photomicrographs of Figure 15, which illustrate three stages of corrosion of a sodium silicate composition containing 43 percent SiO_2 by weight which was attacked by atmospheric moisture under controlled room conditions of 70 percent relative humidity and 70°F . The samples shown from left to right were photographed (a) immediately after removal from the desiccator, (b) 30 minutes later, and (c) 1 1/2 hours later.

The identification of the mechanism of corrosion, and the correlation of corrosion rates with induced physical and chemical changes are currently being studied and will be reported in a separate paper. For the purposes of this work, the accumulated residue shown on the exposed glass surface is believed to be a precipitated alkaline compound which formed on the surface as a non-adherent solid after reaction with either the water or carbon dioxide contained in the atmosphere.

The presence of this residue during a coating run generally resulted in poorly bonded deposits which cracked or spalled during the cooling cycle, presumably because the crystalline contaminant effectively blocked the ability of the plating vapor to form a continuous, chemically bonded film along the glass surface.

Furthermore, the residue usually promoted coating structures which microscopically appeared to exhibit more variability or defect areas than those produced



(A) (B) (C)
Figure 15. Dissolution kinetics of sodium silicate glass by atmospheric attack with time. Exhibit (A): fresh surface.
Exhibit (B): 30 minutes later. Exhibit (C): 90 minutes later. One inch on photographs equals 107
microns.

on clean surfaces. It is uncertain whether these effects are related to heterogeneous nucleation sites or other effects.

It was determined that improved coatings were attained on ground and polished substrates. Those substrates which were not ground and polished generally exhibited some warpage and the surfaces were microscopically undulating. These conditions generally produced non-continuous, variable coatings. Removal of all microscopic contours from the glass surface by grinding to produce a generally flat surface was found to be more important than polishing the surface to a high reflectance level, in terms of the coating quality achieved. These effects may be explained by considering that the residual shear stress components of the film and the glass were decreased by a flat surface. Furthermore, it may be assumed that all mechanically worked surfaces, regardless of the degree of polish, contain some roughness; slightly microscopically roughened surfaces would probably promote coating adhesion.

E. Characterization of SiO_2 Coatings

The highest quality SiO_2 glass films were obtained at deposition temperatures between 1000°F and 1050°F , yielding an average coating growth rate of approximately 4000 Å per hour. Higher deposition temperatures created higher residual stresses in the deposits, and lower temperatures were found to result in excessively slow reaction rates and films which were more clouded in appearance. The films were grown by bubbling nitrogen gas at two cfh through ethyl orthosilicate contained in a flask at room temperature. The substrate was positioned upon one face in the center of the deposition zone approximately three inches from the effluent

end of the input gas tube. The concentration of the reactant gases in the vapor mixture approximated 800 ppm under these conditions, and the efficiency averaged 2 percent.

Figure 16 shows the relationship between deposition temperature and the rate of reaction for SiO_2 coatings. It is noted that the reaction rate reached a maximum at 1150°F and decreased at higher temperatures because of premature decomposition of the plating vapor prior to contacting the substrate.

Various analytical schemes were employed to classify the films obtained. Visual inspection revealed the appearance of a coating which was clear and glassy in nature. This observation was reinforced by microscopic examination, which also brought out the topographical details as seen in Figure 17.

The composition of the film was checked by infrared absorption. The spectra showed a strong absorption band at 9.2 microns and lesser bands at 12.5 and 21.9 microns, thus corresponding with the known bands for silicon dioxide glass (42). No evidence of non-stoichiometric silicon oxide could be found.

X-Ray diffractometer scans showed a broad, diffuse band at 4.3 Å, thus indicating the presence of SiO_2 glass (43). Some of the higher temperature coatings were found to have a slightly crystalline nature. This was generally more prevalent on the bottom face of the substrate where slower deposition rates, higher temperatures, and impurity nucleating sites probably occurred at the interface between the substrate and the substrate holder. Under these conditions, the presence of cristobalite was confirmed by X-Ray analysis. The crystalline material was deposited with a high degree of preferred orientation, as observed by the fact that diffraction occurred for

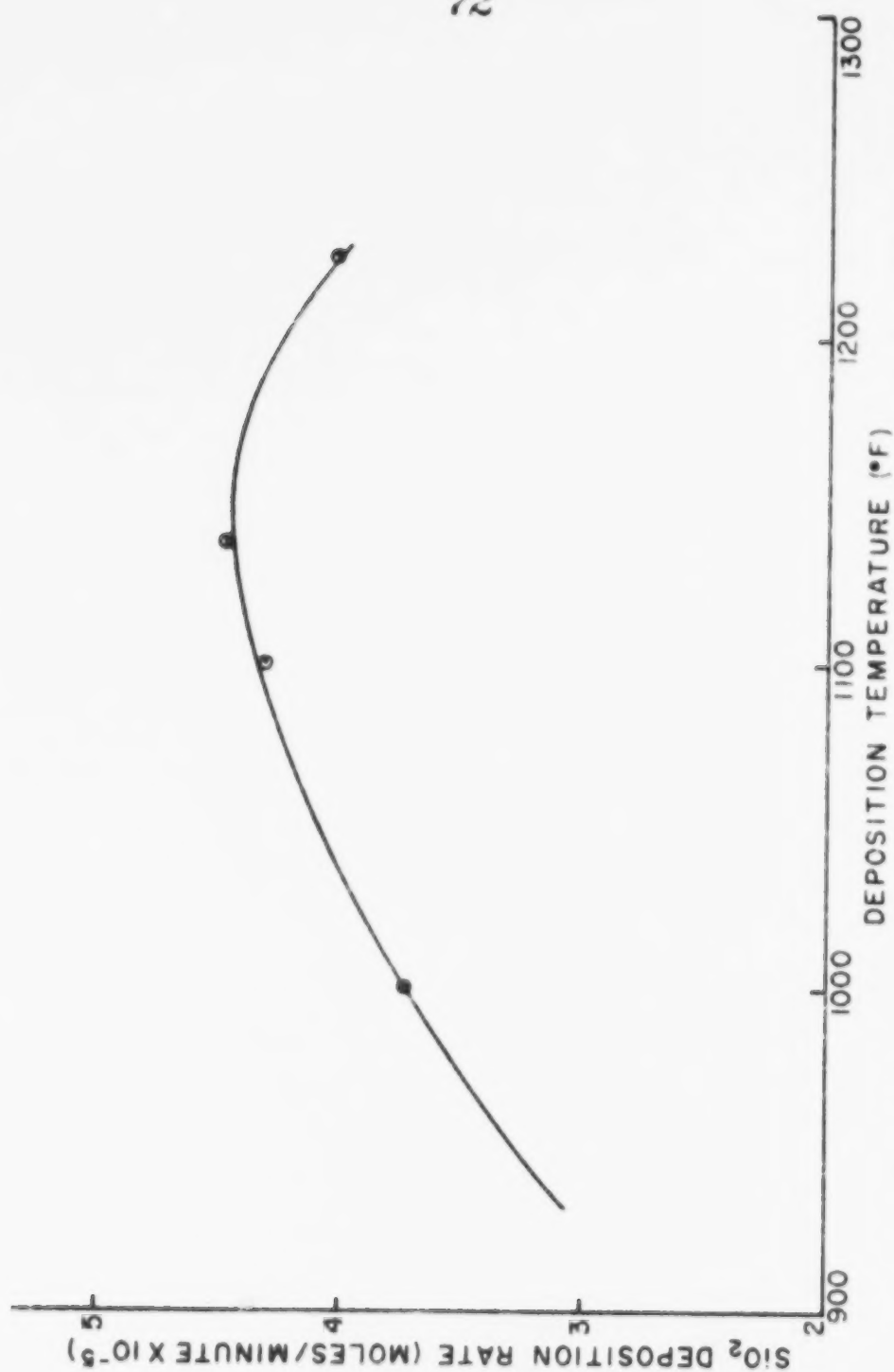


Figure 16. Plot of SiO₂ deposition rates at different deposition temperatures. The data was derived by bubbling nitrogen gas through ethyl orthosilicate at 1 cfm, vaporization temperature 70° F; substrate orientation 3 inches; time 14 hours.

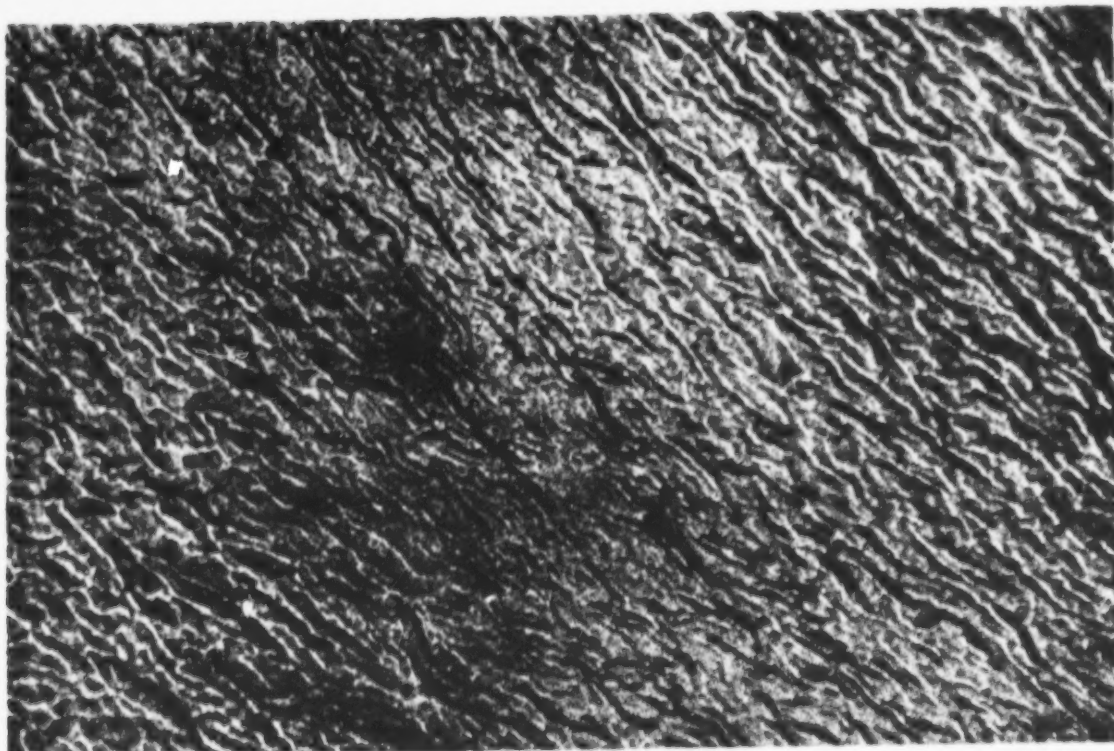


Figure 17. Photomicrograph of surface topography of a typical SiO_2 deposit. The coating was derived by bubbling nitrogen gas through ethyl orthosilicate at 2 cfh; vaporization temperature 70°F ; deposition temperature 1135°F ; substrate orientation 3 inches; time 17 hours. One inch on photomicrograph equals 53.3 microns.

only one of the major intensity peaks for that material--at an interplanar spacing of 4.15 Å. Table IV lists the important diffraction peaks and their intensities for this substance. Optical examination showed the crystals to be large in size, approximately 100 microns in diameter. Figure 18 depicts several cristobalite crystals which have grown and coalesced together. No crystals of comparable size were found on the top face of the substrate.

Figure 19 reveals the curious appearance of a columnar growth habit which was found to typify fractured samples, as well as the presence of an interlocking (mechanical) bond at the interface on roughened substrate surfaces. Based on the excellent adherence of SiO_2 coatings on smooth as well as rough surfaces, it is believed that the basic source of bond strength is derived from a chemical bond.

The SiO_2 as shown by Table V, exhibited a high degree of chemical inertness. In order to measure this property, films were microscopically observed before and after 30 minute soaks in 50 percent concentrated sulfuric, nitric, hydrochloric, and acetic acids, as well as in sodium hydroxide. No chemical deterioration was observed in these media. Only hydrofluoric acid was found to degrade the film, and it could be removed very rapidly by exposure to this material.

F. Characterization of TiO_2 Coatings

Whereas optimized SiO_2 coatings were obtained under a somewhat limited range of conditions, such was not the case for TiO_2 coatings, as previously discussed. Furthermore, it was determined that TiO_2 could generally be deposited in either crystalline or amorphous form at faster rates and with lower residual stresses developed at the substrate interface than SiO_2 . Consequently, it was determined at the outset

TABLE IV

X-RAY DIFFRACTION DATA FOR COATINGS OBTAINED (44)

CRYSTALLINE MATERIAL	MINERALOGICAL NAME	INTERPLANAR SPACING AND RELATIVE INTENSITIES OF THREE STRONGEST LINES SPACING, (Å) RELATIVE INTENSITY	HANNAWALT CARD FILE INDEX NUMBER
SiO ₂	Cristobalite	4.15	4-0359
		2.53	
		1.64	
TiO ₂	Anatase	3.51	4-0477
		1.89	
		2.38	
Ti ₂ O ₃	Titanium Sesquioxide	1.68	2-1359
		0.90	
		1.85	



Figure 18. Photomicrograph of cristobalite crystals. The coating was derived by bubbling nitrogen gas through ethyl orthosilicate at 2 cfh; vaporization temperature 70°F ; deposition temperature 1220°F ; substrate orientation 3 inches; time 11 hours. One inch on photomicrograph equals 53.3 microns.

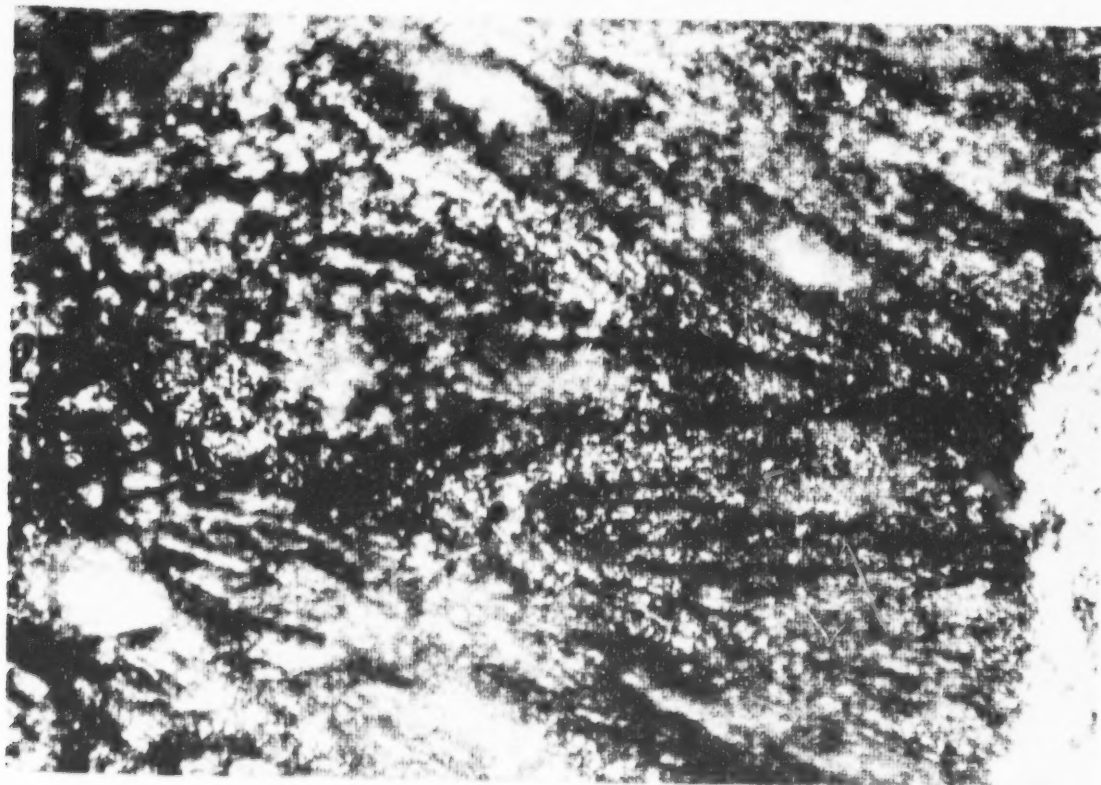


Figure 19. Photomicrograph of SiO_2 coating--substrate interface showing columnar growth habit of SiO_2 . The substrate is oriented below the coating. The coating was derived by bubbling nitrogen gas through ethyl orthosilicate at 1 cfh; vaporization temperature 70°F ; deposition temperature 1050°F ; substrate orientation 3 inches; time 48 hours. One inch on photomicrograph equals 53.3 microns.

CHEMICAL DURABILITY OF COATINGS OBTAINED

COATING TESTED	CORRODING AGENT	EFFECT
SiO ₂ glass	H ₂ SO ₄	Insoluble
	HNO ₃	Insoluble
	HCl	Insoluble
	HC ₂ H ₃ O ₂	Insoluble
	HF	Soluble
	NaOH	Insoluble
TiO ₂ amorphous	H ₂ SO ₄	Insoluble
	HNO ₃	Insoluble
	HCl	Insoluble
	HC ₂ H ₃ O ₂	Insoluble
	HF	Insoluble
	NaOH	Insoluble
TiO ₂ anatase	H ₂ SO ₄	Insoluble
	HNO ₃	Insoluble
	HCl	Insoluble
	HC ₂ H ₃ O ₂	Insoluble
	HF	Insoluble
	NaOH	Insoluble

of this work that TiO_2 should make a good candidate for coating soluble glass, if not alone then certainly as a prime coat for a composite coating composed of, for example, TiO_2 and SiO_2 . In the latter case, it is believed that the TiO_2 would buffer the stress distribution over two interfaces rather than one, and would also probably enhance the overall protective characteristics of the overlay barrier. Corollary studies in these areas are currently in progress and will be discussed in a subsequent paper.

For applications as either single or composite coatings, the use of extremely thin, uniform, amorphous TiO_2 films would be desired because they would be least objectionable from an optical standpoint. Because of the wide divergence in refractive indices between substrate and coating, interference colors become prominent as the thickness increases over 1000 Å. An amorphous, uniform film in this thickness range would reduce the overall light transmission through the piece, which would appear tinted to the eye. Crystalline films, however, would tend to reflect the light by scattering, thus decreasing the light transmission to an even greater extent. Unfortunately, no method was devised to retain the amorphous structure of TiO_2 prime coats during the subsequent SiO_2 deposition at higher temperatures, and the amorphous phase was ruled out except for external coating applications.

The structure of the deposits obtained over a range of conditions was studied by X-Ray diffraction. The structure of the TiO_2 deposits was found to depend primarily upon deposition temperature and to a lesser extent upon the mass flow rate of

the reactant vapor. Figure 20 illustrates the relationship between these two structure determining variables as derived from a systematic investigation of approximately one hundred samples. The boundary line, however, is shown hatched because its accuracy is believed to be limited to plus or minus 25° F. The transition between amorphous and crystalline deposits was found to occur at 620° F plus or minus 25° F for the range of tetraisopropyl titanate mass flow rates investigated. Coatings formed below the transition line were amorphous and those above were crystalline. Curiously, the transition temperature was found to decrease at extremely low mass flow rates, and several samples analyzed in that range were found to contain various oxygen deficient modifications of TiO_2 , principally Ti_2O_3 . Crystalline deposits derived from higher mass flow rates were all stoichiometric. Table IV contains the essential X-Ray diffraction data for the crystalline forms of titanium oxide found in this study.

The stoichiometric crystalline deposits consisted of preferentially oriented anatase. This fact was established by examining the location and intensities of the three major diffraction peaks for that material and comparing the data to that produced during an actual X-Ray scan. Two of the three lines, at interplanar spacings of 3.51 Å and 1.89 Å could always be identified; the line at 2.38 Å was always characteristically absent, thus indicating preferred orientation of the deposit.

High quality, uniform thin films of TiO_2 were readily produced by bubbling nitrogen gas at ten cfm through tetraisopropyl titanate maintained in a temperature-controlled flask at 212° F. The substrate was vertically positioned inside the center

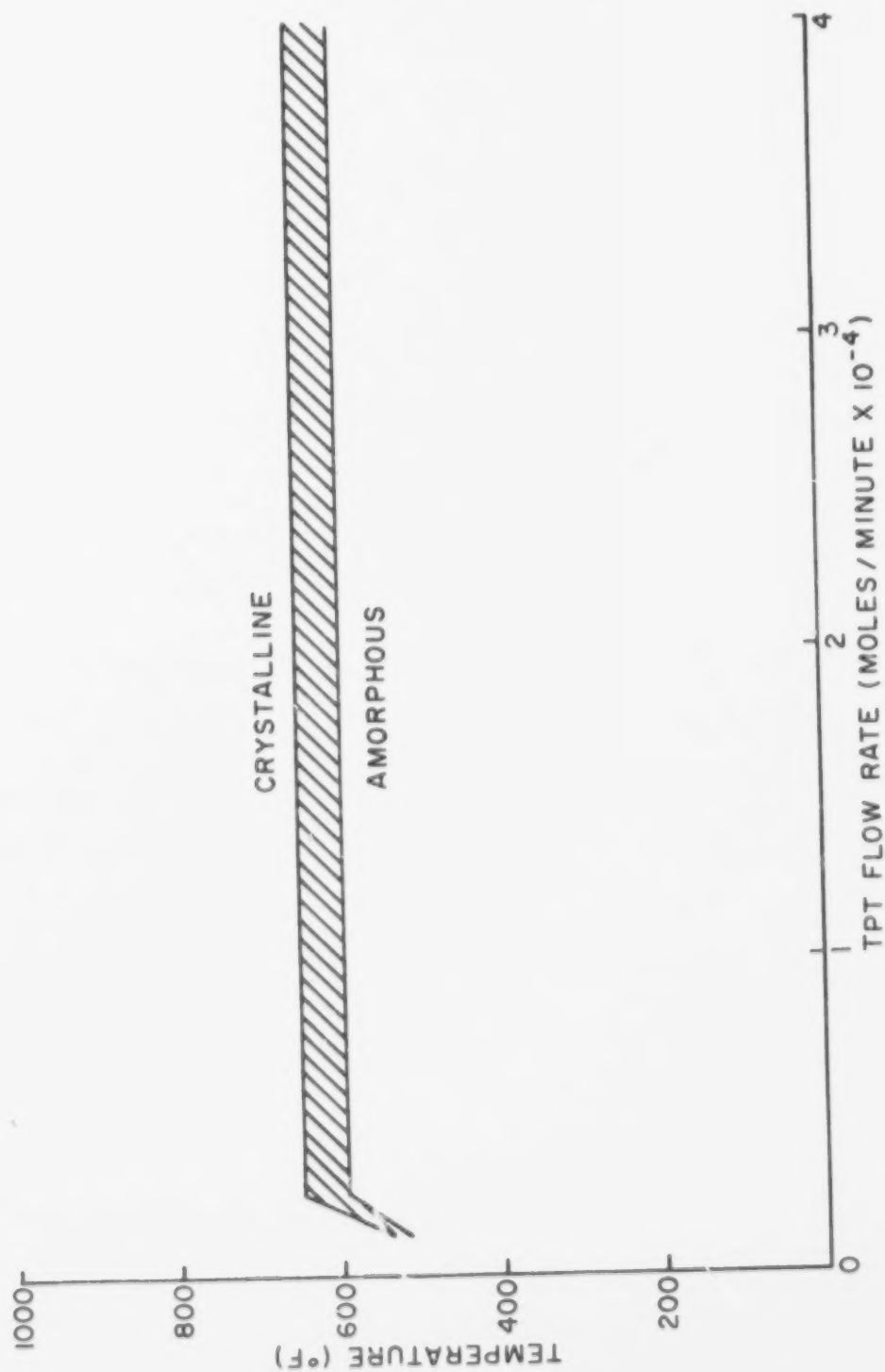
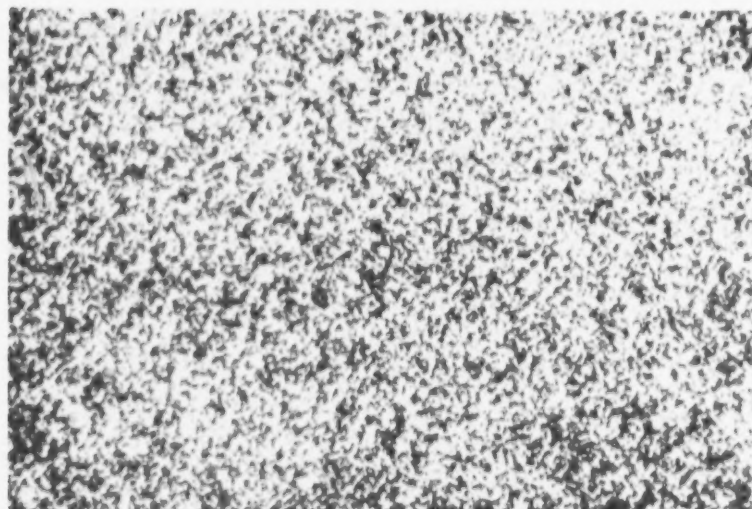
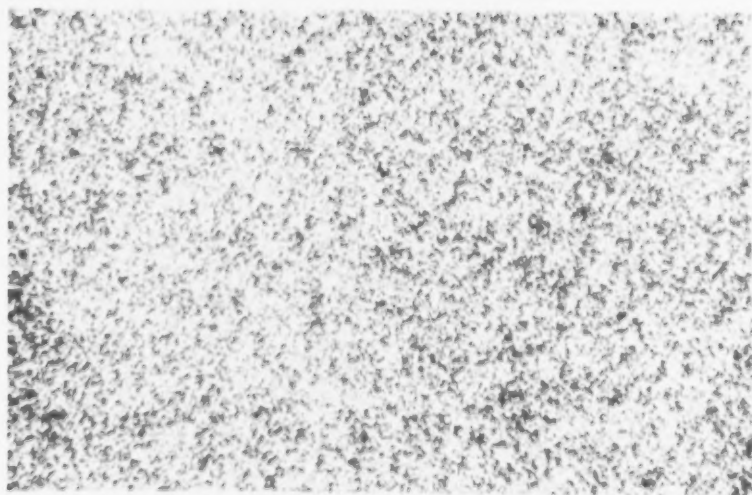


Figure 20. Plot of TiO_2 structures at different temperature and reactant vapor mass flow rates

of the deposition zone with its front face perpendicular to the impinging gas stream issuing from the end of the input tube ten inches away. Although the coating efficiencies were low (less than 3 percent), the uniformity of the coatings was excellent and the associated film properties such as adherence and chemical inertness were quite good between 500°F - 800°F . The conditions described allowed amorphous coatings to be formed at the lower temperatures at growth rates of approximately 4000 Å per hour, and crystalline films were produced at the higher temperatures at growth rates of approximately 6000 Å per hour.

The overall microstructural uniformity of the crystalline deposits was very sensitive to the coating conditions used. Many of the crystalline samples produced were found to contain obvious variations when viewed under the microscope. Several of the most extreme conditions have previously been mentioned in conjunction with coatings that cracked or spalled when subjected to a concentrated, poorly mixed vapor. More typically, the variations observed were much more subtle, as shown in Figure 21, which depicts two regions of the same sample. Exhibit (A) was taken from an area which received the direct impact of a poorly diffused, reactant vapor-rich gas stream resulting in many small grains. Exhibit (B) was located on the periphery of this impinging stream and consequently received less cooling effect as well as a more dilute dosage of reactant vapor. It is characterized by a lesser number of larger grains. The effects to be expected from a consideration of the principles of nucleation and grain growth are exactly as represented by the two microstructures shown.



(A) (B)
Figure 21. Typical anatase microstructures taken from different areas of same sample. Exhibit (A) received a more concentrated dosage of reactant vapor than Exhibit (B), but was also cooled more by the impinging gas stream. The photomicrographs were derived by bubbling nitrogen gas through TPT at 10 cfh; vaporization temperature 70° F; deposition temperature 690° F; substrate orientation 4 inches; time 60 minutes. One inch on photomicrograph equals 88.9 microns.

Crystalline coatings which were slowly grown were sometimes found to contain one and two dimensional growth features incorporated into the deposit. Figure 22 shows two examples of dendritic growth.

A general characteristic of the TiO_2 coatings was their smooth, continuous appearance. This was especially true for the amorphous films, as shown by Figure 23. This photomicrograph shows a cracked film with some portions stripped away to reveal the substrate. It was selected to portray the effects denoted above, which are readily brought out because of the visual contrast.

Figure 24 shows an interesting view of a duplex coating. In this instance, two 15,000 Å layers of TiO_2 were deposited around a 45,000 Å layer of SiO_2 . The photomicrograph indicates that both coatings were applied evenly and continuously.

The chemical durability of the TiO_2 films was observed and generally found to be excellent. The same reagents employed for measuring the chemical inertness of the SiO_2 coatings were used for both amorphous and crystalline TiO_2 . The results are shown in Table V.

G. Other Coatings

Several runs were made with ethyltriethoxysilane as the source material for the SiO_2 coatings. The coatings were applied in a similar manner to the SiO_2 films derived from ethyl orthosilicate, except that the optimum temperature of deposition was slightly higher, around 1200° F - 1250° F. Oily traces of partially

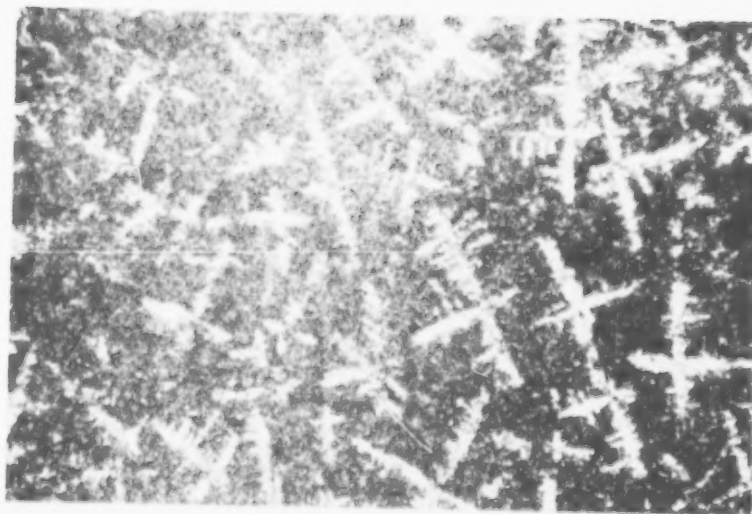
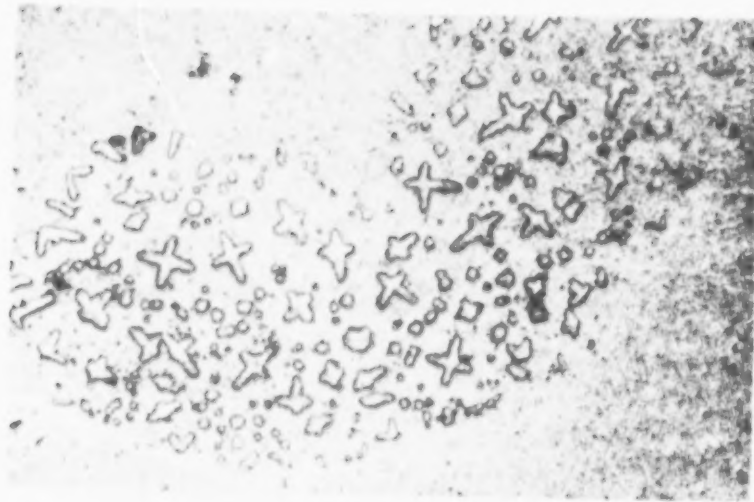


Figure 22. Photomicrographs of secondary growth features in TiO_2 deposits. Exhibit (A): dendrites. Exhibit (B): crosses. These coatings were derived by bubbling nitrogen gas through TPT at 10 cfm; vaporization temperature 700 F; deposition temperature 9760 F; substrate orientation 4 inches; time 60 minutes. One inch on photomicrograph equals 88.9 microns.

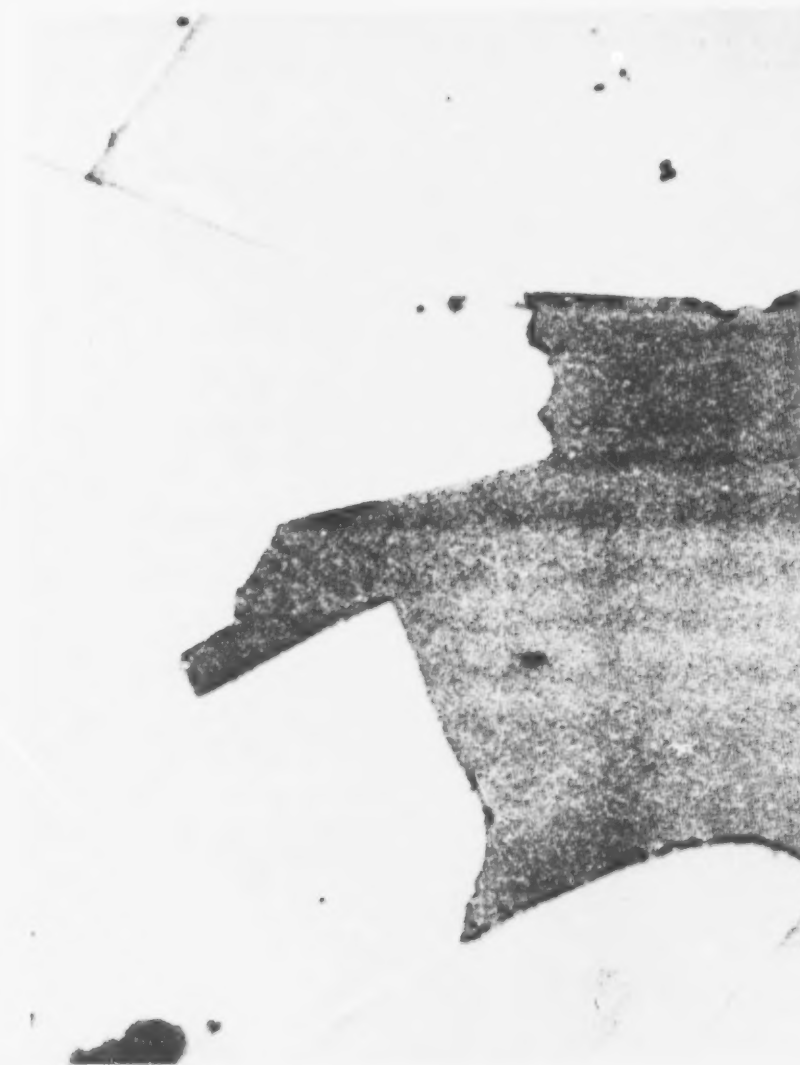


Figure 23. Photomicrograph of surface topography of amorphous TiO_2 film. Coating was derived from nitrogen gas bubbled through TPT at 10 cfh; vaporization temperature 212°F ; deposition temperature 620°F ; substrate orientation 4 inches; time 5 minutes. One inch on photomicrograph equals 53.3 microns.

TiO₂ ---

SiO₂ ---

TiO₂ ---

Substrate ---



87

Figure 24. Photomicrograph of a duplex coating. Structure is composed of two 15,000 Å layers of TiO₂ with 45,000 Å layer of SiO₂ sandwiched between. The TiO₂ coatings were derived by bubbling helium gas through TPT at 9 cfm; vaporization temperature 70° F; deposition temperature 700° F; substrate orientation 4 inches; time 3 hours. The SiO₂ coating was derived by bubbling helium gas through ethyl orthosilicate at 4 cfm; vaporization temperature 70° F; deposition temperature 1100° F; substrate orientation 3 inches; time 12 hours. One inch on photomicrograph equals 53.3 microns.

decomposed silane could be found inside the combustion tube for lower deposition temperatures. No differences were observed in the SiO_2 films produced from the two different materials. Because of this factor and the significantly higher unit cost of the silane, it was not explored further.

Aluminum oxide was deposited from aluminum isopropoxide vapors at deposition temperatures between 550°F - 700°F . The deposits obtained were apparently amorphous Al_2O_3 . The isopropoxide was not easily vaporized in the flask that was used for the other plating agents, primarily because of the fact that the material required heating to 223°F in order to melt it. The coating process used resembled the technique employed for coating substrates with TiO_2 . The deposition rates were slower, however. Al_2O_3 low deposition temperature coatings offer some potential, and should be investigated further.

H. Initial Corrosion Studies

Since the various films produced on Pyrex microslides were found to be highly resistant to boiling water as well as other corrosive media, the major remaining question concerning the utility of the films revolves around their ability to form a continuous, impenetrable barrier between the soluble glass and the corrodant. A thorough analysis of this important subject is currently in progress and will be reported on at a later date. Nevertheless, several tentative observations may be made at this point, based on experimental runs made during this study.

Uncoated soluble glass discs were readily dissolved in tap water between room temperature and the boiling point of water. The rate of dissolution was found

to be highly sensitive to the amount of alkali in the glass, the temperature of the water, and the amount of agitation. Typically, 57 percent sodium oxide and 43 percent silicon dioxide compositions were completely dissolved in less than 15 minutes by agitated cold tap water, whereas the most resistant composition containing 43 percent Na_2O typically required over 90 minutes to accomplish the same task. However, water at 140°F was found to completely dissolve the two compositions in less than five minutes, and 30 minutes, respectively.

The application of both SiO_2 and TiO_2 coatings to these materials was found to increase the durability substantially. Generally, however, there appeared to be a very wide variation in the protective quality of both types of films. Some, in fact deteriorated almost as rapidly as if they were uncoated while others demonstrated an ability to withstand the ravages of 140°F water for several hours without deteriorating.

It is thought that any break or discontinuity in the film structure allows moisture to attack the interfacial bond between the substrate and the coating at a localized point. Once initiated, the process spreads rapidly across the entire surface, destroying the protective film.

CONCLUSIONS

1. The coating apparatus designed and constructed for this investigation is a sound laboratory tool, capable of producing many types of chemically deposited coatings over a range of controlled conditions. Its utility is not restricted to this particular system; rather, it has a broad capability for research work in many areas of this technology, such as diffusion masking for semiconductors, and others.
2. Soluble silicate glass compositions are readily coated by chemical vapor deposition processes. The surface condition of the glass must be closely controlled in order for satisfactory coatings to result.
3. Metallic oxides derived from selected organic esters provide excellent coating materials for soluble glass substrates. The high vapor pressure and chemical stability of the mother liquid readily allows coatings to be produced by pyrolysis reactions at the heated substrate surface.
4. Titanium oxide coatings are readily produced over a wide range of controlled conditions such as deposition temperature, time, carrier gas flow rate, reactant vapor concentration, substrate orientation, and others. The coatings produced can be amorphous or crystalline, depending upon conditions. These coatings are chemically stable, and form a chemical bond with the glass surface.

5. Silicon oxide glass coatings are produced under somewhat more restricted conditions; however, the coatings formed likewise possess excellent properties. The problem of residual stress in the coated sample is a greater hazard with SiO_2 coatings because of generally higher deposition temperatures and a greater mismatch of thermal expansion coefficients.
6. The high residual stress level contributes to microscopic defects in the finished coatings. Generally uncontrollable coating conditions also promote defects. These are typified by variable vaporization rates, non-uniform dispersion of the vapor species, uneven substrate temperatures, variable substrate surfaces, and impurities.

RECOMMENDATIONS FOR FUTURE WORK

The feasibility of ultimately applying the technology derived from this investigation to the solution of glass container waste control problems is bright; however, many basic problems have been found which must be solved in the laboratory prior to significant scaled-up operations becoming a reality.

The significance of this work was that it demonstrated that oxide coatings may be readily applied to soluble silicate glass substrates by chemical vapor deposition processes with some flexibility in the selection of process parameters used. This represents in itself an important early finding, fundamental to much of the work which will follow. Corollary studies are presently being pursued in the areas of glass corrosion kinetics, mechanical properties, and other types of coating media. As rapidly as possible, new information must be disseminated to all interested parties, to assure that the central objective of the overall project remains in focus and that wasted motion is minimized.

The major product deficiencies denoted in this work were coated specimens characterized by high residual stresses and variable microstructures. The author believes that these problems must be resolved prior to further significant advances in this area. The solutions may involve new materials systems, equipment modifications, new procedures of coating, or a combination of all. In all likelihood, each of the corollary study areas will be correspondingly affected by any changes that take place.

In terms of the specific problems just recounted, a high residual stress level obviously damages the mechanical and chemical durability properties of the composite structures. A need exists to more closely match the thermal expansion coefficients of the materials used in order to decrease these effects. As a general class of materials, the oxides do not match up satisfactorily with the glass compositions used; in fact, the residual stresses for several coatings produced in this study were calculated and found to exceed the theoretical mechanical stress limits of the substances involved. The mechanism of stress relief which allowed the coating and substrate to remain intact is unknown at the present time, but the example clearly illustrates the point.

Alternately, methods may be devised to coat substrates at much lower temperatures. Klerer (45) has reported that amorphous SiO_2 films may be readily formed from the vapor phase at deposition temperatures as low as 150°F - 250°F by going through a radical-coupling step. This technique would represent an interesting solution to the problem and should be investigated.

It is surmised that the variability that currently exists in the coating microstructures is at least partially responsible for the erratic tentative results which have been obtained from an early study of the corrosion rates of the coated samples. Defects have been microscopically observed in many coatings at relatively low magnification; this suggests that the defects which are likely present on a truly microscopic scale as well are producing pinholes and other faults which are the early failure points during a corrosion evaluation.

9.1 The question remaining to be answered is how to effectively minimize or even erase these variations. The author believes that the problem of structural defects can be largely defeated by devising an improved vaporizer and vapor delivery system. A basic requirement in this process is that the substrate must receive a constant, well-mixed and diffused vapor supply to all surfaces. It is well known that local concentrations of reactant vapor in the total vapor stream under the influence of elevated temperatures will upset the thermodynamic balance of the system and possibly cause growth defects to occur during the growth process.

Another area which should be upgraded is that of input materials. Higher purity coating reagents than the ones employed in this work should be obtained and used for future studies if possible. Special precautions should be installed to minimize contamination at all levels and from all potential sources. The soluble silicate substrates must be prepared with particular emphasis placed on mixing uniformity, annealing, and surface condition. It is believed that each of these items plays some part in determining the relative number of defects in a coating.

Solution of these problem areas would provide a giant step in the right direction. Still remaining, however, is the matter of basic cost. The process is obviously inherently expensive, and the investigator is limited in the possible significant approaches that might defray costs. During the course of this study, few conditions were explored that yielded a coating efficiency above 10 percent. The best coatings that were produced were less than 5 percent, in fact. Reclaim systems would elevate this figure somewhat, but the basic cost factors such as expensive plating agents, sophisticated control equipment, highly trained

operators, and the like probably point to a basic problem which can only be improved upon by diligent effort--not solved completely. To illustrate this last point, compressed dry air should suffice as a substitute for the carrier gases employed, thus resulting in some savings.

The author believes that a logical long range approach to the program at this stage of its development would be to design a glass composition which might be dissolved by the elements, as at a refuse dump, over a period of several months' duration. This composition would likely possess a lower expansion coefficient than the ones used in this work; consequently, it is likely that a stress-compatible coating system could be worked out easier for this material, and the resultant coated product would thereby possess improved mechanical properties. Since the durability of the glassy material would also likely be upgraded to a significant degree, it is possible that the coating microstructural sensitivity factor would be correspondingly reduced, growth defects might be less critical, and thinner (cheaper) coatings would thereby suffice. This approach seems to make more practical sense at the present time than any other.

LITERATURE CITED

1. Breidenbach, A.W., "Research Activities Of The Solid Wastes Program Of The Public Health Service--A Status Report," U.S. Department of Health, Education and Welfare, Washington, D.C., 1-2, (1968).
2. President's Science Advisory Committee's Report Of The Environmental Pollution Panel, "Restoring The Quality Of Our Environment," Washington, D.C., 141, (November, 1965).
3. Glass Industry, 92 (1): 40, (1968).
4. Alexander, T., "Where Will We Put All That Garbage?" Fortune Mag. 126 (5): 151, (1967).
5. Anonymous, "Municipal Refuse Disposal," American Public Works Association, 47-52, (1966).
6. Anonymous, "Proceedings Of The National Conference On Solid Waste Research," American Public Works Association, (1963).
7. Morey, G.W., The Properties Of Glass, Reinhold Publishing Corp., New York, (1954).
8. Vail, J.G., Soluble Silicates: Their Properties And Uses, Volume II, Reinhold Publishing Corp., New York, (1952).
9. Vail, J.G., Soluble Silicates: Their Properties And Uses, Volume I, Reinhold Publishing Corp., New York, (1952).
10. Plunkett, J.D., "NASA Contribution to the Technology of Inorganic Coatings," NASA SP-5014 Technology Survey, Washington, D.C., (1964).
11. Powell, C.F., "Chemical Vapor Deposition," Vapor Deposition, Edited by C.F. Powell, J.H. Oxley, and J.M. Blocher, Jr., John Wiley and Sons, Inc., New York, (1966).
12. Blocher, J.M., Jr., "The Promise And Problems Of Chemical Vapor Deposition," Chemical Vapor Deposition, Defense Metals Information Center Report 170, Battelle Memorial Institute, Columbus, Ohio, (1962).
13. Accountius, O.E., "Vapor Deposition," Critical Evaluation Of Ceramic Processing At Subconventional Temperatures, Edited by S.D. Brown, Air Force Materials Laboratory Report TR-67-194, Wright-Patterson Air Force Base, Ohio, (1967).

14. Powell, C.F., Campbell, I.E., and B.W. Gonser, Vapor Plating, John Wiley And Sons, Inc., New York, (1955).
15. Powell, C.F., Oxley, J.H., and J.M. Blocher, Jr., Vapor Deposition, John Wiley And Sons, Inc., New York, (1966).
16. Sawyer, W.E., and A. Man, U.S. Patent 229, 335 (June 29, 1880).
17. Aylsworth, J.W., U.S. Patent 553,296 (January 21, 1896).
18. deLodyguine, A., U.S. Patent 575,002 (January 12, 1897).
19. Krier, C.A., "Protective Coatings," Vapor Deposition, Edited by C.F. Powell, J.H. Oxley and J.M. Blocher, Jr., John Wiley And Sons, Inc., New York, (1966).
20. Blocher, J.M., and J.H. Oxley, "Chemical Vapor Deposition Opens New Horizons In Ceramic Technology," Bull. Am. Ceram. Soc., 41 (2): 81-84, (1962).
21. Walton, D., "The Orientation Of Vapor Deposits," Phil. Mag., 82 (7): 1671-1679, (1962).
22. Secrist, D.R., and J.D. Mackenzie, "Identification Of Uncommon Non-crystalline Solids As Glasses," J. Am. Ceram. Soc., 48 (9): 487-91, (1965).
23. Sinclair, R.W., "Inorganic Glass Films--Their Preparation, Properties, And Uses," The Glass Industry, 92 (1): 22-28, (1968).
24. Holland, L., The Properties Of Glass Surfaces, John Wiley And Sons, Inc., New York, (1964).
25. Anonymous, "Tyzor Organic Titanates," E.I. Dupont deNemours And Co., Wilmington, Del.
26. Deyrup, A.J., U.S. Patent 2,881,780 (April 22, 1958).
27. Badger, A.E., U.S. Patent 2,881,566 (April 14, 1959).
28. Powell, C.F., "Chemically Deposited Nonmetals," Vapor Deposition, Edited by C.F. Powell, J.H. Oxley, and J.M. Blocher, Jr., John Wiley and Sons, Inc., New York, (1966).

29. Oxley, J.H., "Transport Processes," Vapor Deposition, Edited by C.F. Powell, J.H. Oxley, and J.M. Blocher, Jr., John Wiley And Sons, Inc., New York, (1966).
30. Li, C.H., "Epitaxial Growth Of Silicon," J. Electrochem. Soc., 109 (10): 952-57, (1962).
31. Jordan, E.L., "A Diffusion Mask For Germanium," J. Electrochem. Soc., 108 (5): 478-81, (1961).
32. Vasicek, A., Optics Of Thin Films, Interscience Publishers, Inc., New York, (1960).
33. Powell, C.F., "Stresses In Deposits," Vapor Deposition, Edited by C.F. Powell, J.H. Oxley, and J.M. Blocher, Jr., John Wiley and Sons, Inc., New York, (1966).
34. Hirth, J.P., "Condensation Processes," Vapor Deposition, Edited by C.F. Powell, J.H. Oxley, and J.M. Blocher, Jr., John Wiley and Sons, Inc., New York, (1966).
35. Coffin, L.F., "Structure-Property Relations For Pyrolytic Graphite," J. Am. Ceram. Soc., 47 (10): 473-78, (1964).
36. Gretz, R.D., "Structure Of Deposits," Vapor Deposition, Edited by C.F. Powell, J.H. Oxley, and J.M. Blocher, Jr., John Wiley and Sons, Inc., New York, (1966).
37. Handbook Of Organometallic Compounds, Edited by H.C. Kaufmann, D. Van Nostrand Company, Inc., New York, (1961).
38. Handbook Of Chemistry and Physics, Edited by R.C. Weast, The Chemical Rubber Company, Cleveland, O., (1967).
39. Turnbull, R.C., and W.G. Lawrence, "The Role Of Titania In Silica Glasses," J. Am. Ceram. Soc., 35 (2): 48-53, (1952).
40. Sosman, R.B., The Properties Of Silica, Reinhold Publishing Corp., New York, (1927).
41. Engineering Properties Of Selected Ceramic Materials, Edited by J.F. Lynch, C.G. Ruderer, and W.H. Duckworth, The American Ceramic Society, Columbus, O., (1966).
42. Pliskin, W.A., "The Evaluation Of Thin Film Insulators," Thin Solid Films, 2 (1): 1-26, (1968).

43. Law, H.B., "The Formation Of Insulating Layers By The Thermal Decomposition of Ethyl Silicate," The Review Of Scientific Instruments, 20 (12): 958, (1949).
44. Index To The X-Ray Powder Data File, Edited by Joseph V. Smith, ASTM Special Technical Publication 48-H, American Society For Testing Materials, Philadelphia, Pa., (1959).
45. Klerer, J., "A Method For The Decomposition Of SiO_2 At Low Temperatures," J. Electrochem. Soc., 108 (11): 1070-71, (1961).

DETERMINATION OF PLATING VAPOR CONCENTRATION IN THE CARRIER GAS STREAM

For the purposes of this illustration, assume that it is desired to obtain the concentration of tetraisopropyl titanate (TPT) in nitrogen gas flowing through the system at a rate of two cubic feet per hour.

1. Calculate the number of moles of carrier gas utilized per unit of time, using the following relationship from the ideal gas law:

$$n_g = \frac{PV}{RT}$$

where n = the number of moles of carrier gas
 P = pressure in atmospheres
 V = volume in liters per unit of time
 R = universal gas constant
 T = temperature in degrees Kelvin

It may be assumed that the carrier gas is exhausted to the atmosphere for purposes of calculation. The universal gas constant expressed in the choice of units used is 0.082 $\frac{\text{liter-atmospheres}}{\text{mole-degree K.}}$. The volume is

given in cubic feet per hour and must be converted to liters per hour by a conversion factor of 28 liters per cubic feet. Substituting in the equation yields

$$n_g = \frac{(1) (2 \times 28)}{(0.082) (300)} = 2.2 \text{ moles of nitrogen gas per hour}$$

2. The next step is to determine the amount of TPT used during that time interval. This is determined by weighing the flask before and after the specified time interval. Assuming that 3.8206 grams of TPT were

used, one may divide this number by the molecular weight of TPT to determine the number of moles of TPT used.

$$n_{\text{TPT}} = \frac{\text{weight loss in grams}}{\text{molecular weight}} = \frac{3.8206}{284.2} = 0.0134$$

3. The resultant concentration is expressed as the ratio of the number of moles of plating compound to the number of moles of carrier gas.

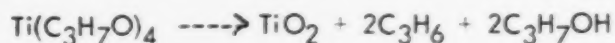
$$C = \frac{n_{\text{TPT}}}{n_{\text{g}}} = \frac{0.0134}{2.2} = 0.0061$$

The resultant gas stream is composed of 6.1 parts of TPT to 1000 parts of carrier gas or 6100 parts per million (ppm).

DETERMINATION OF COATING EFFICIENCY

For the purposes of this illustration, assume that the coating efficiency of TPT is required during a run.

1. Determine the loss in weight of the vaporizer containing the liquid plating substance. Assume that this loss amounts to 4.7394 grams of TPT over a given period of time.
2. Determine the gain in weight of the substrate during the same period of time. Assume that this gain is 0.0731 grams of TiO_2 .
3. Write a balanced chemical equation for the reaction taking place to compute the yield of the reaction, that is, the number of moles of TiO_2 formed by the pyrolysis of 1 mole of TPT.



In this case, one mole of TiO_2 is formed from one mole of TPT, or expressing it in terms of molecular weights, 1 mole of TiO_2 (79.9 grams) is created every time 1 mole of TPT (284.2 grams) is decomposed. Expressed as a fraction, the TiO_2 yield from the reaction is simply $\frac{79.9}{284.2} = 0.281$

4. Multiply the TiO_2 yield fraction by the number of grams of TPT vaporized to obtain the number of grams of TiO_2 contained in the TPT that vaporized. For this example,

$$(4.7394) (0.281) = 1.332$$

5. The coating efficiency is expressed as a fraction of the TiO_2 contained in the vaporizing TPT divided into the TiO_2 deposited on the substrate. For this run,

$$\text{Coating Efficiency} = \frac{0.0731}{1.332} = 0.548 = 5.48\%$$

DETERMINATION OF RESIDUAL COATING STRESS

If a substrate and coating are under isothermal conditions during application, and the thermal expansion coefficients of both vary in approximately the same manner, the coating stress S_T , induced by thermal variations in a coating applied to a flat plate, assuming no plastic flow occurs, can be estimated (33):

$$S_T = \frac{E_B E_C \Delta T (\alpha_B - \alpha_C)}{E_B + 2E_C (t_C / t_B)}$$

where

S_T = coating stress in pounds per square inch

E_B = elastic moduli of base in pounds per square inch

E_C = elastic moduli of coating in pounds per square inch

ΔT = temperature change from deposition temperature, in degrees Fahrenheit

α_B, α_C = linear thermal expansion coefficients of the base and coating respectively, in reciprocal degrees Fahrenheit.

t_C, t_B = thickness of the coating and base respectively, in inches

If $\Delta T (\alpha_B - \alpha_C)$ is positive, a tensile stress will be induced in the coating and a compressive stress in the substrate. If the term is negative, the reverse will occur.

PART II

MECHANICAL PROPERTIES OF WATER-SOLUBLE SODIUM SILICATE GLASSES

A method for mechanically testing sodium silicate glass by the bending test was presented. Five glass compositions between $1.0\text{Na}_2\text{O} \cdot 1.0\text{SiO}_2$ and $1.0\text{Na}_2\text{O} \cdot 1.6\text{SiO}_2$ are investigated. The strength was examined as a function of four variables: composition, re-anneal time, atmospheric exposure, and coatings.

This work represents the second segment of a two year investigation to determine a feasible method of processing glass containers after use.

The description of fabricating and testing rectangular glass bars $3/8'' \times 3/8'' \times 4''$ was described, with the author's interpretation of the results.

Sodium silicate glasses between the composition range $1.0\text{Na}_2\text{O} \cdot 1.3\text{SiO}_2$ and $1.0\text{Na}_2\text{O} \cdot 1.6\text{SiO}_2$ possess adequate strength to be utilized as a container material. However, only after the completion of concurrent studies on dissolution kinetics and coatings can a just appraisal of the feasibility of this project be made.

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INTRODUCTION

The use of glass has so saturated the market of commodities distribution, that glass has become one of the largest and most troublesome constituents of solid waste disposal. The high chemical durability that glass possesses makes it indispensable in the containment of corrosive systems, but renders it a formidable opponent on the trash heap. The formulation and design of a glass container whose durability and susceptibility to environments can be controlled would greatly assist in the degradation of such containers.

The solubility of sodium silicate glasses has been observed as a natural oddity in the field of glass technology. Morey (1) points out that special attention should be called to the $\text{Na}_2\text{O} \cdot 2\text{SiO}_2$ quartz eutectic. There is a remarkable melting point lowering of about 1000°F after the addition of 25% Na_2O . The low temperature of this eutectic is of vital importance to glass technology. More importantly, Morey suggests that glass of this composition would be excellent "were it not easily attacked by water."

If a suitable coating could be developed that provided an impenetrable barrier for water vapor, certain sodium silicate glass could be utilized as container material.

This paper is the second in a series of papers that investigates the feasibility of using sodium silicate glass as a method of improving the degradation of solid waste by rendering glass easily disposable.

REVIEW OF LITERATURE

Glass making is older than recorded history. No one can say when or where or who first discovered how to make glass. Perhaps the discovery resulted from an experiment, but more likely the discovery was accidental. At some time in history the conditions existed where someone heated sand and soda over a hot fire and upon cooling discovered this vitreous substance - glass.

Solid Waste Disposal

The United States is facing a staggering problem in trying to dispose of the immense amounts of solid wastes that are the unwanted residue of our nation's achievements in production and consumption. Our cities and their surrounding urbanized areas are already bearing the brunt of our explosive growth and increased industrial activity. This country has to deal with 3.5 billion tons of solid waste each year. This consists of 48 billion cans, 26 billion bottles, more than 30 million tons of paper, 4 million tons of plastics, and 100 million rubber tires weighing a million tons (2, 3). With this soaring problem in solid waste disposal becoming more critical, the general public is not aware of the problem. A vivid illustration of public apathy can be seen in the attitude toward the non-returnable glass bottles which relieves the producer, distributor, and consumer of handling cost and inconvenience, but creates more burden for refuse collectors. It is unfortunate that most people are not aware of the additional problems that have been created by this convenience item. The refuse collector

is aware of his increased burden, however, and the use of non-returnable bottles is increasing at an alarming rate (4).

Initial action was instigated by passage of the Solid Waste Disposal Act of 1965, Title II of Public Law 89-272, which President Johnson signed on October 20 of that year. This new legislation directs the Secretary of Health, Education, and Welfare to initiate, encourage, and support a national program aimed at discovering and evaluating better methods of coping with the solid waste problem (5, 6).

Containers, with respect to solid waste disposal procedures, can be divided into two classifications: combustible and non-combustible. Containers made from paper, wood, or plastic are the major portion of the organic compounds of refuse. Combustible containers have heat value and when dry will burn freely in incinerators without forced draft and without fuel.

A non-combustible container is any container that is unburnable at ordinary incinerator temperatures (1300° to 2000°F). Although metal containers undergo slow disintegration by oxidation, this process is far too slow to be employed in connection with incinerator procedures. Carelessly stored, used containers are aesthetically objectionable and may harbor rodents and other vermin. Open cans and bottles catch and hold water in which mosquitoes can breed, so that many individual citizens unknowingly but actively encourage the proliferation of these disease carrying pests (7).

Funds and leadership for research and planning programs to curb the undesirable effects of inadequate solid waste control are starting to be provided (8). Essential to this effort is a method of processing

incombustible, unreactive glass containers after use. The potential impact to such a development upon solid waste control may be readily visualized by considering that approximately one hundred thirty-five glass bottles and jars alone are produced each year for every person in the United States. This amounts to twenty-six billion glass containers each year (3). The control of the disposal of glass would be a tremendous step toward the control of all solid waste.

Soluble Silicate Glasses

With the development of glass blowing techniques, the formulation of glass containers was directed to yield high chemical durability. The resistance which glass offers to various corrosive agents is of great practical significance. Morey (1) points out that the chemical durability of glass is often times the chief reason for its preference over competing materials.

There are six important types of glass used today: soda-lime, lead alkali, borosilicates, aluminosilicates, 96% silica, and fused silica. The most common kind of glass is soda-lime-silica glass composed of silica sand, soda, ash, and limestone. The addition of increasing amounts of soda to silica while decreasing other constituents significantly lowers the melting and softening temperatures. However, the chemical resistance is also impaired, and if enough soda is used the glass is readily attacked by many environments (1).

In the past the properties of alkali silicate glasses, like sodium silicate glass, have been investigated more from scientific curiosity than from practical scientific investigation. Soluble silicates have been desired more for other industrial uses than for glasses. They

have been used for such applications as adhesives, cleansers, cements, deflocculants, and protective coatings (9).

The alkali silicate glass system would offer some inherent advantages if adopted for glass container production. Vail (9) points out that sodium silicate gels are now added to polluted water as a flocculant in the settling and filtration steps of water purification. At the same time these gels form solutions that tend to form a thin film on the inside of water pipes which protect them against water corrosion. These are important by-products of soluble silicates.

Morey (1) has the most complete record of the investigation of sodium silicate glasses. However, the range of his investigation is limited between 100% SiO_2 - 0% Na_2O and 70% SiO_2 - 30% Na_2O , and this did not extend into the range of compositions under investigation. Morey points out that with the high SiO_2 composition, a sodium disilicate ($\text{Na}_2\text{O} \cdot 2\text{SiO}_2$) is formed that is easily made into a glass, while as the soda content increases, a second compound is formed: sodium metasilicate ($\text{Na}_2\text{O} \cdot \text{SiO}_2$). It has been shown by a number of workers (10, 11, 12) that the range of glass formation in the Na_2O - SiO_2 system is continuous from SiO_2 to a limiting composition close to that of the metasilicate $\text{Na}_2\text{O} \cdot \text{SiO}_2$. The limiting composition depends on the experimental conditions. As is to be expected, the smaller the melt and the greater the rate of cooling, the higher the Na_2O content at which the material can still be made as glass free from any crystalline material. The work of Moore and Carey (11), working with 6 gram melts, established the limiting composition as 47 mole percent Na_2O . Imaoba and Yamazaki (12), in a general survey of glass forming regions in simple silicate

systems, found it possible to make glasses containing up to 58.8 weight percent Na_2O (57.8 mole percent) on a scale of 1-2 grams. The different results for the $\text{Na}_2\text{O}\cdot\text{SiO}_2$ system clearly show the effect of the scale of melting, and illustrate the importance of specifying as clearly as possible the melting and cooling conditions when reporting the region glass formation in a system. It may be significant that the limit in the $\text{Na}_2\text{O}\cdot\text{SiO}_2$ system coincides almost exactly with the composition at which Na_2O becomes the primary crystalline phase, that is, the first phase to crystallize from the melt. At this composition a change will occur in the nature of the crystallization process which will be reflected in the kinetics of the process. Scholes (13) substantiates the fact that sodium metasilicate can be obtained as a glass, but only in small quantities. However, to meet the specifications necessary for use in the container industry, it is only necessary for these glasses to meet the qualifications of a water soluble container and not those that make it a glass.

Physical Properties

The knowledge of the physical properties of sodium silicate glass is somewhat limited. There have only been a few researchers that have done extensive work with these glasses because its solubility has greatly hindered any thorough investigation. Not only have the investigations been limited, but they have produced significant discrepancies in these researchers' results. Some properties that are easier to obtain than others have been sufficiently substantiated. These include changes in density, refractive index, and linear thermal expansion below and above the transformation temperature. These properties are

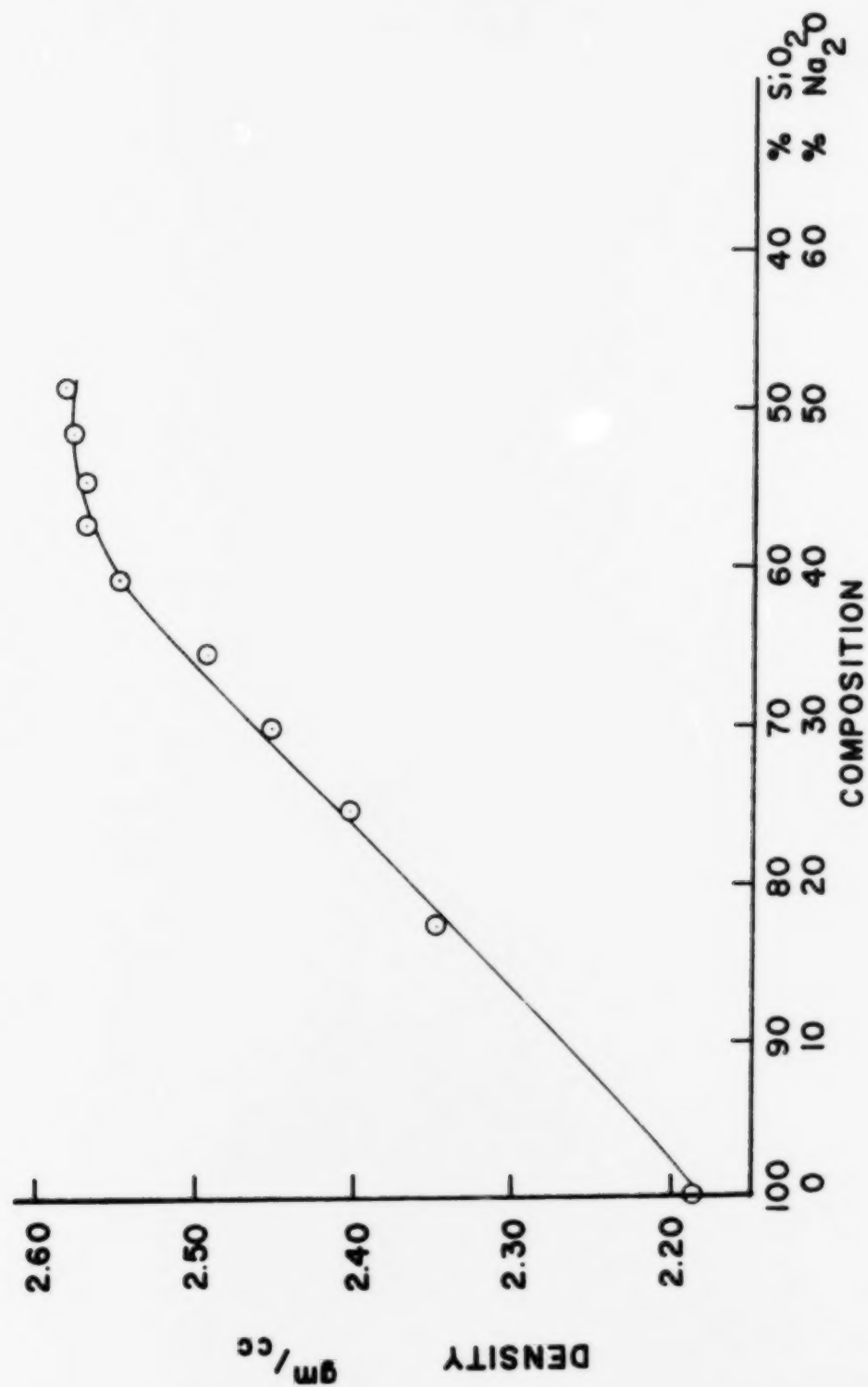


FIGURE 1. DENSITY VS COMPOSITION

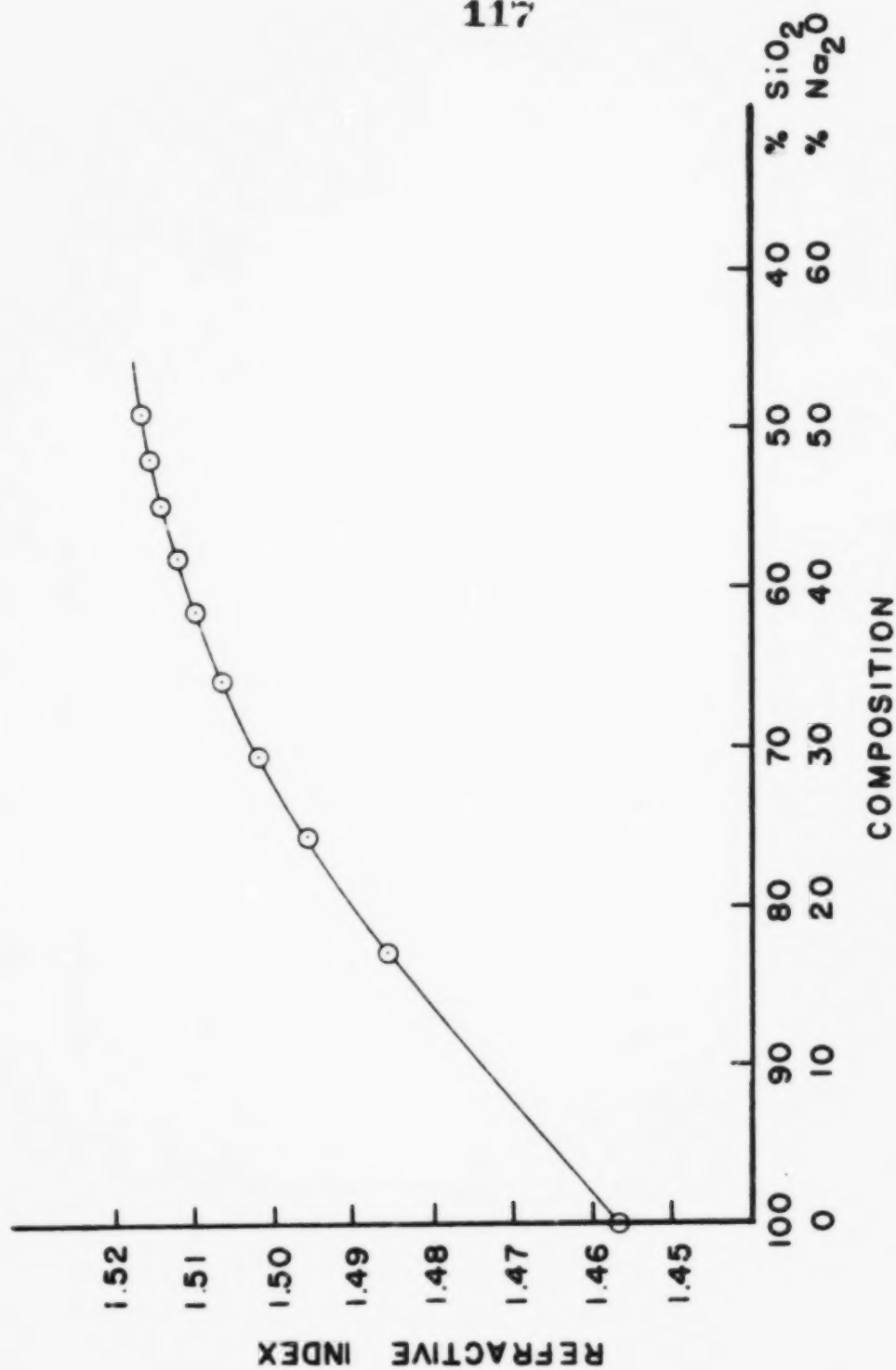


FIGURE 2. REFRACTIVE INDEX VS. COMPOSITION

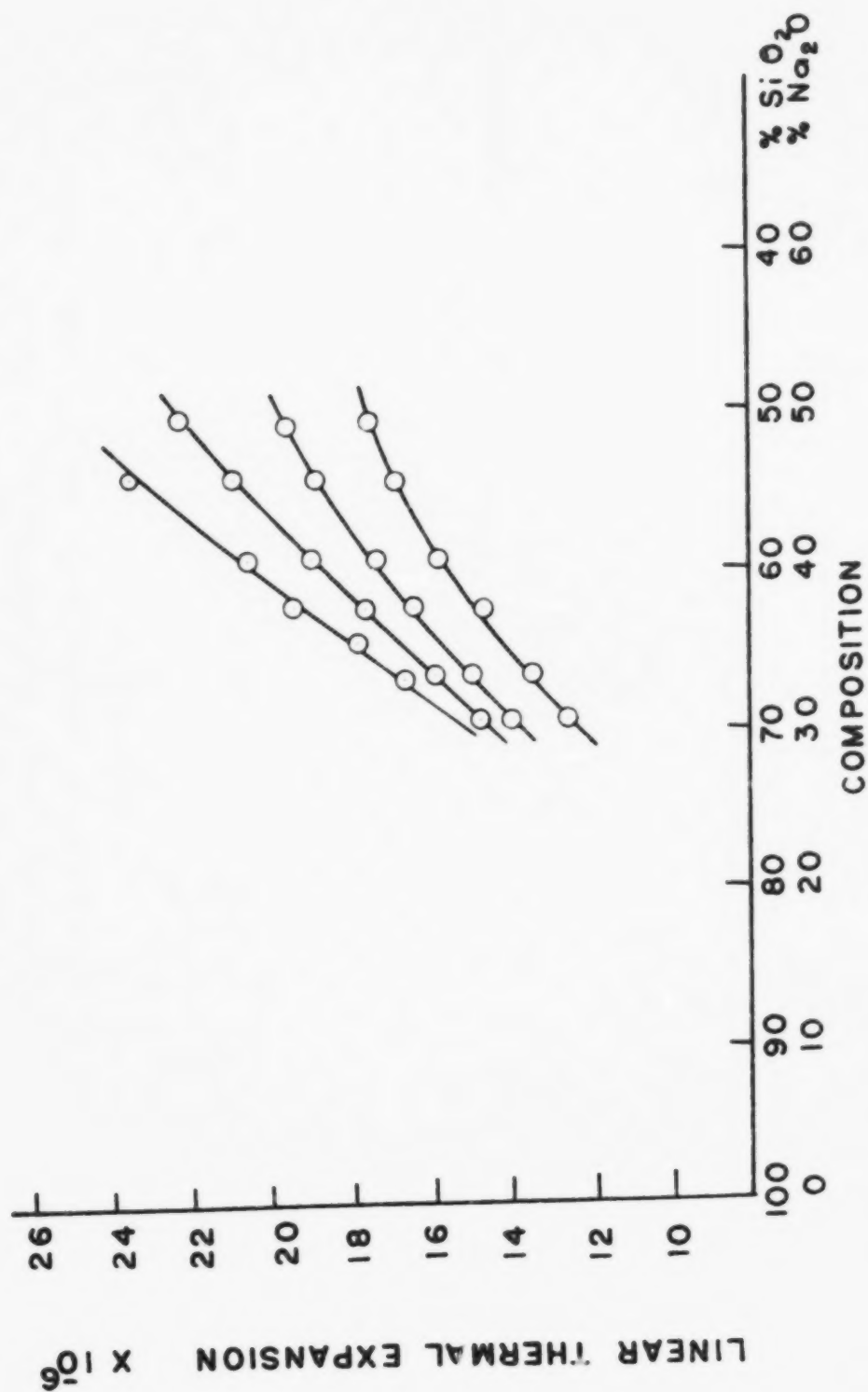


FIGURE 3. LINEAR THERMAL EXPANSION BELOW THE TRANSFORMATION TEMPERATURE.

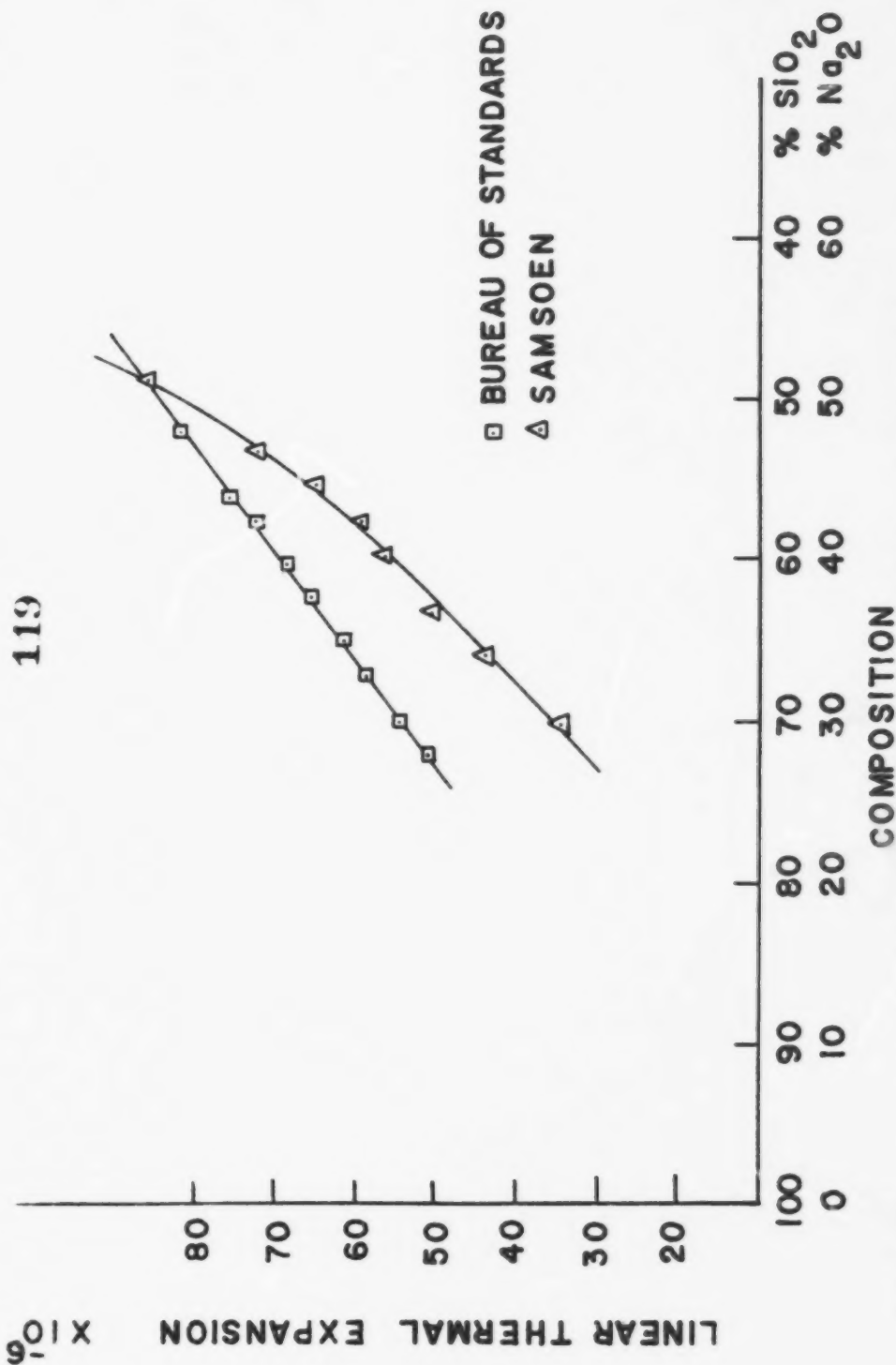


FIGURE 4. LINEAR THERMAL EXPANSION ABOVE THE TRANSFORMATION TEMPERATURE

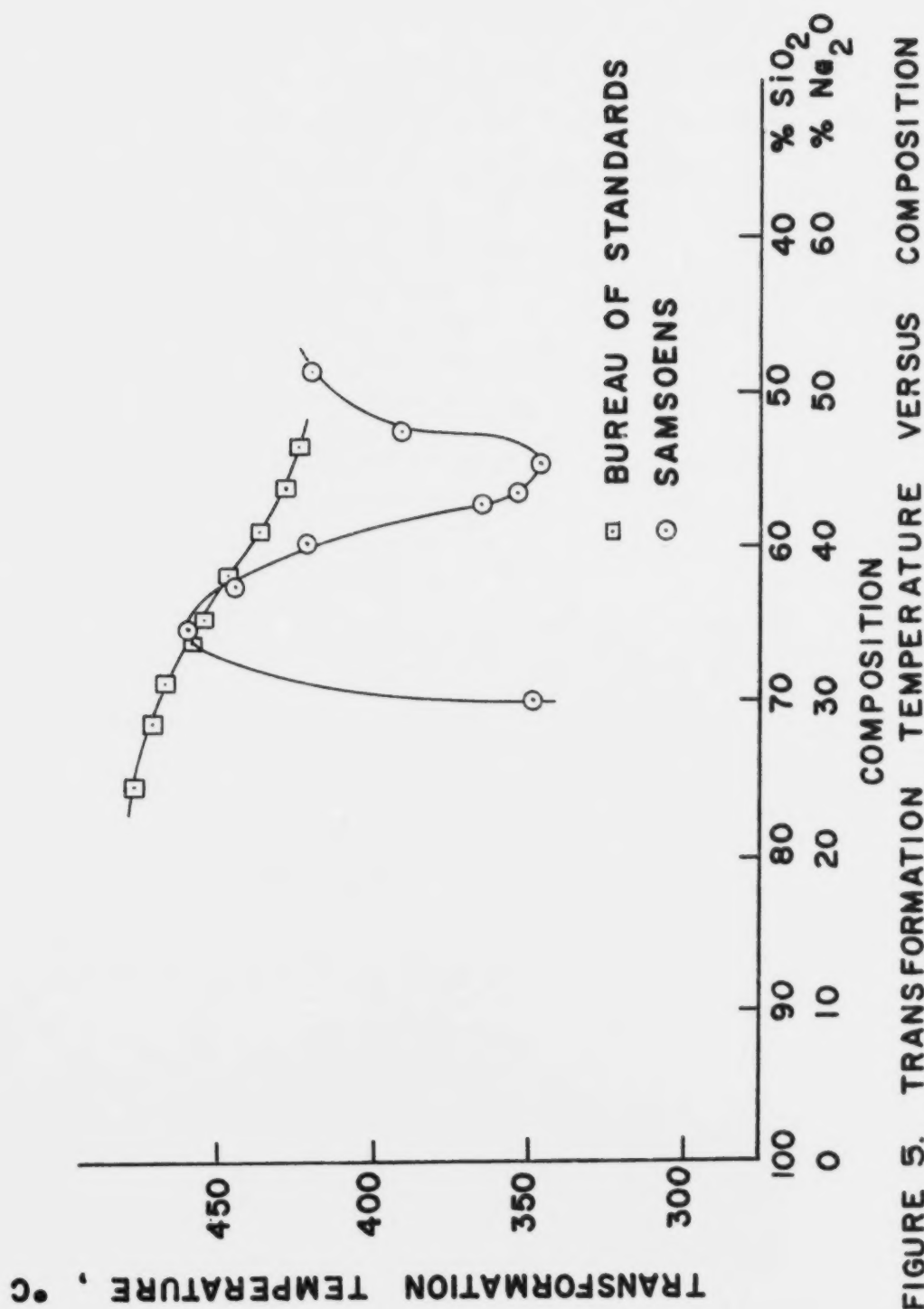


FIGURE 5. TRANSFORMATION TEMPERATURE VERSUS COMPOSITION

shown in Figures 1, 2, 3, and 4 respectively and are taken from Morey (1). An example of the discrepancies in results is seen in Figure 5 which shows the change in the transformation temperature with changes in composition. The results from Samsoens (14) and the Bureau of Standards (1) are used.

Strength of Glass

"Even when conducted with utmost care, studies of the mechanical properties of glass are plagued by what seems to be an inherent and unavoidable scatter, a condition stemming from the susceptibility of the glass surface to flawing by either mechanical or chemical action (15)."

It is practically impossible to predict the strength of a particular specimen of glass, except within very broad limits. Only the average obtained from a large number of strength measurements has real significance. An average strength figure alone does not characterize the property measured since it is also necessary to know the extent to which individual measurements are likely to depart from the mean. This fact makes it necessary to approach the measurement of the strength of glass with a statistical procedure.

It is widely accepted that glass fails only under tensile stresses. The strength of glass is conditioned by the existence of flaws or weak points in the material. Several observations regarding the strength of glass are summarized below.

- (1) The strength of a massive glass specimen measured by bending or tension experiments is much less than predicted by any theory which assumes that strong inter-molecular forces co-operate in a regular way.

- (2) The strength of similar pieces of glass broken in tension may vary widely and only average figures hold any significance.
- (3) The strength of glass is easily affected by the treatment of the material, and in particular the factors affecting the conditions of the surface, such as environments, and annealing times and temperatures.

The Griffith Flaw Theory (24) provides an explanation for the difference between the theoretical strength and the experimentally observed results from the presence of small cracks or flaws around which a strong stress concentration arises when the solid is stressed. The first and third statements above can be used to substantiate the Griffith Flaw Theory. The strength of massive glass specimens may also vary as a function of the geometrical shape and size. Holland and Turner (16) have shown that for specimens tested in bending, the flexural strength decreases as the thickness is increased.

In summary, any attempt to find the strength of glass as a function of any other parameter is a very difficult task. Some (17) feel that there is no correlation among glass parameters, such as strength versus composition, while there are others (1, 19, 20, 21, 23) that disagree.

Measurement of Strength

Two methods can be used to measure strength of brittle material. The most direct way to measure strength is to take a rod or fiber with enlarged ends and load it with a gradually increasing weight until the

specimen breaks. If the cross sectional area of the specimen is A , and the load is W , then the nominal breaking stress is W/A . The value of W/A obtained by this method of testing will usually be much greater for fine fibers than for large rods due to the greater probability of encountering a flaw in a larger cross sectional area than a smaller one. The direct measurement of tensile strength by rod or fiber method is not so convenient as the indirect method using a bending test. For the direct test it is necessary to work with specimens with enlarged ends while with the bending test it is not.

A rod can be easily tested by bending it under a load and simply measuring the load required to break the specimen. If the load W pounds is applied at the center of a span L inches in length, the maximum bending moment developed is $WL/4$ inch-pounds. This maximum bending moment occurs in the cross section of the beam directly under the load, that is, at the center of the span. If the section modulus of the cross section is A , then the maximum tension developed is $WL/4A$. This parameter is called the 'modulus of rupture.' Assuming the beam to be symmetrical above and below the central axis, the value of A will be $2I/d$, where I is the flexural moment of Inertia, and d is the depth of the beam. For different geometrical configuration the value of A will change. In the rectangular specimen used, the value of A is $bd^2/6$ where b and d are the specimen dimensions respectively, and the value of the modulus of rupture for rectangular beams is $3WL/2bd^2$.

As Scholes (13) emphasized in his work on the strength of glass, the beam may not break directly under the load, where the stress is greatest, but at some other point along the span. This happens because

in glass the weakness of its surface is being tested, and not the strength of the bulk samples. This fact holds more importance when a glass, like the sodium silicate glass, is attacked by the constituents of the atmosphere.

Rudnick, Hunter, and Holden (21) used a third method for determining the strength of brittle materials, that of the diametral-compression test. However, this is limited to a specific fracture pattern.

OBJECTIVES OF RESEARCH

The basic objective of this research was to expand the knowledge of the mechanical properties of sodium silicate glass. This work represents the second segment of a projected two year study which will deal with the feasibility of, and methods for, the degradation of glass packaging containers. The research was composed of three phases.

The initial phase concerned a method of fabricating suitable test specimens that when tested would yield representative mechanical data. This included the selection of methods for testing.

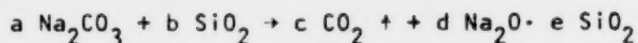
The second phase concerned physical testing of specimens and the interpretation of results. This was achieved by relating strength as a function of four variables: composition, anneal time, exposure time, and coatings.

The final phase involved a critical assessment of the present procedure and recommendations for certain changes in both the method and procedure. The basic limitations of present methods are discussed with ideas for future research presented.

EXPERIMENTAL PROCEDURES

Melt Preparation

The preparation of melts consisted of mixing the desired quantity of Baker Analyzed Reagent Grade Na_2CO_3 and Pennsylvania Pulvarizing Company's highest quality silica. The ratio necessary to yield the desired composition was calculated from the basic equation:



where a, b, c, d, and e are the molar ratio determined by the desired composition. The percent by weight for the five compositions investigated are given in Table I.

The preparation was accomplished by weighing out the desired quantities of material and thoroughly mixing them in a mortar and pestle. The mixture was initially fired in common fireclay crucibles. However, erosion of the crucible at the glass-air interface necessitated the use of another crucible material. The selection was a high quality alumina crucible. The desired composition and the alumina crucibles were heated slowly in a silicon carbide resistance furnace to reduce the problem of thermal fracture to the crucible. After the melting temperature of 1250°C was reached, this temperature was maintained for a minimum of sixty minutes to allow for adequate soaking.

Specimen Fabrication

The fabrication of adequate test specimens proved to be the most formidable obstacle encountered. Initially, cylindrically shaped disks one and one-half inches in diameter and approximately three-eighths of

TABLE I

COMPOSITION BY WEIGHT
OF GLASSES INVESTIGATED

GLASS COMPOSITION	WT % SiO_2	WT % Na_2O
1.0 Na_2O · 1.0 SiO_2	49.2	50.8
1.0 Na_2O · 1.1 SiO_2	51.6	48.4
1.0 Na_2O · 1.2 SiO_2	53.7	46.3
1.0 Na_2O · 1.3 SiO_2	55.6	44.4
1.0 Na_2O · 1.6 SiO_2	60.7	39.3

an inch thick were cast in the steel mold shown in Figure 6. These disks were made to fulfill a three-fold purpose. It was hoped that these disks could be used as a suitable sample to determine strength through diametral testing, solution rates, through rate of dissolution, and to determine the degree of workability of the glass. These disks proved unsatisfactory for the diametral testing technique because they broke with the pattern that was not typical for tensile failure. The diametral compression test is limited to only tensile failures so another testing method had to be utilized. Other test methods were investigated for strength determination even though the disks continued to be used for solubility studies. ASTM, industry, and other researchers (17, 18, 19, 20) provided several testing methods for the modulus of rupture of glass but these tests were for sheets of glass and were not applicable. The lack of correlation between the strength of bulk samples and the strength of fibers tested in tension prevented the use of tensile testing fibers.

The bending test was then chosen to yield strength in the form of modulus of ruptures (MOR). This was accomplished by molding rectangularly shaped bars and breaking these bars in three point loading. The initial material used for the mold was graphite because it was readily available and glass does not wet it. Another mold of mild steel was later made. Several molds were made in an attempt to find a practical size. It was decided that bars three-eighths inch by three-eighths inch by four inches could both be adequately fabricated and tested. Figures 7 and 8 show specimens being molded in both types of molds.

Initially the bars were of poor quality as seen in Figure 9. How-



Figure 6. Photograph of initial disk mold.



Figure 7. Photograph of a disk specimen being poured.



Figure 8. Photograph of bar specimen being poured.

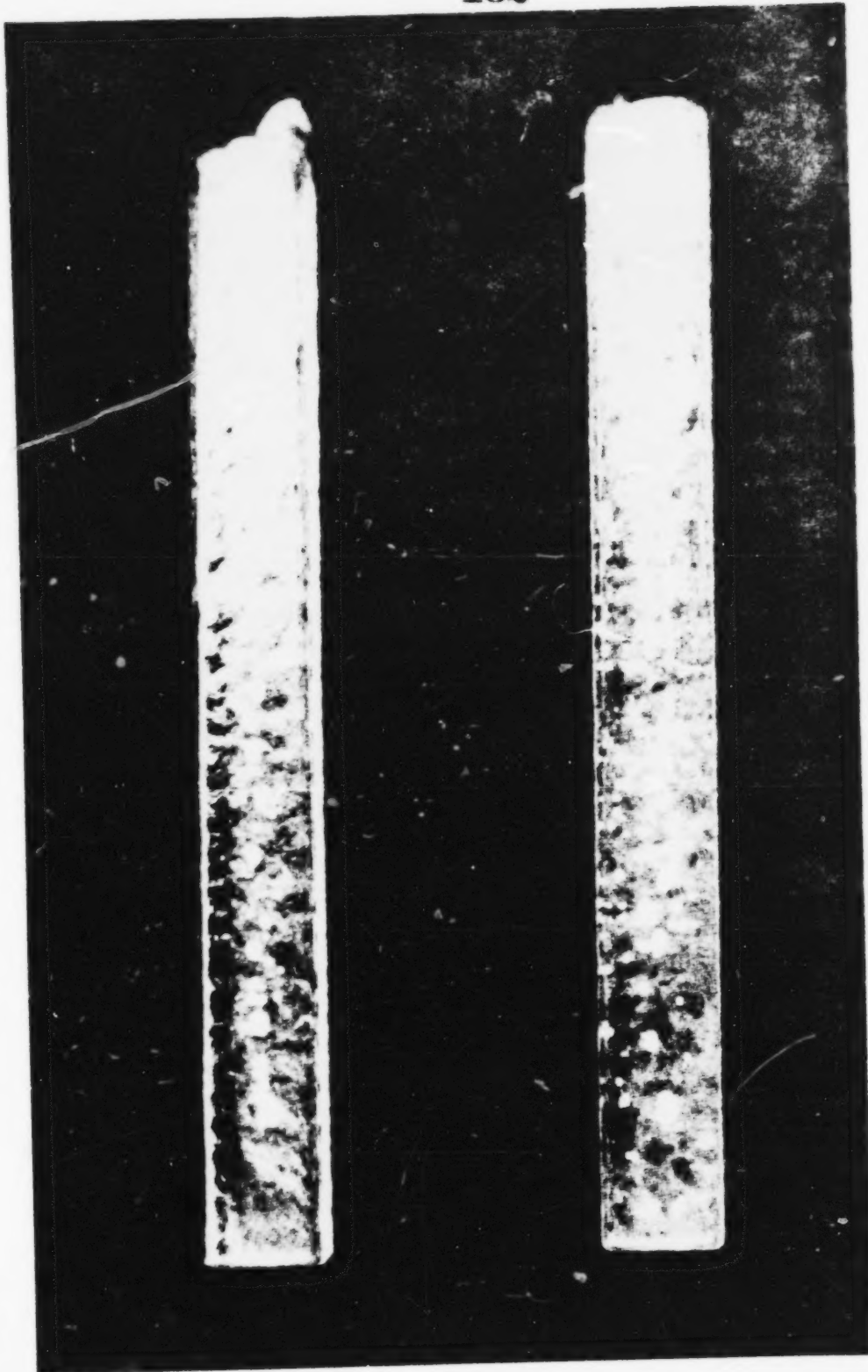


Figure 9. Photograph of the bubble defects encountered in initial test specimens.

ever, as the proper technique was developed the quality improved. No fining agent was needed in the earlier melts because the disk specimens were pressed with sufficient force to squeeze the bubbles from the glass. No provision was made to press the rectangular specimens so 2% by weight of As_2O_3 was added to help sweep the bubbles from the melt. Figure 10 shows the effect of various amounts of As_2O_3 on the incidence of bubbles.

During the initial attempts to mold the disk specimens, the mold was heated by a gas or electric heater to raise the temperature of the mold close to that of the annealing temperature. However, this had no effect on the quality of the test specimens so the heater was removed. After the glass specimens were cast, they were immediately placed in an annealing furnace and held at the annealing temperature suggested by Morey and listed in Table II. The annealing temperature was maintained for thirty minutes and then the furnace was shut down and allowed to cool with the specimen inside. Upon reaching atmospheric temperature, the furnace was opened and the samples were removed and placed in a desiccator for storage and transportation to the testing area.

The three point bending method was used for the bending test. This was performed on a Baldwin-Tate-Emery testing machine. A span of two inches, and a loading rate of .05 inches/minute was used. The data was collected on the basis of readings to the nearest pound.

The same procedure was used for the preparation, fabrication, annealing, and storage of all specimens tested.

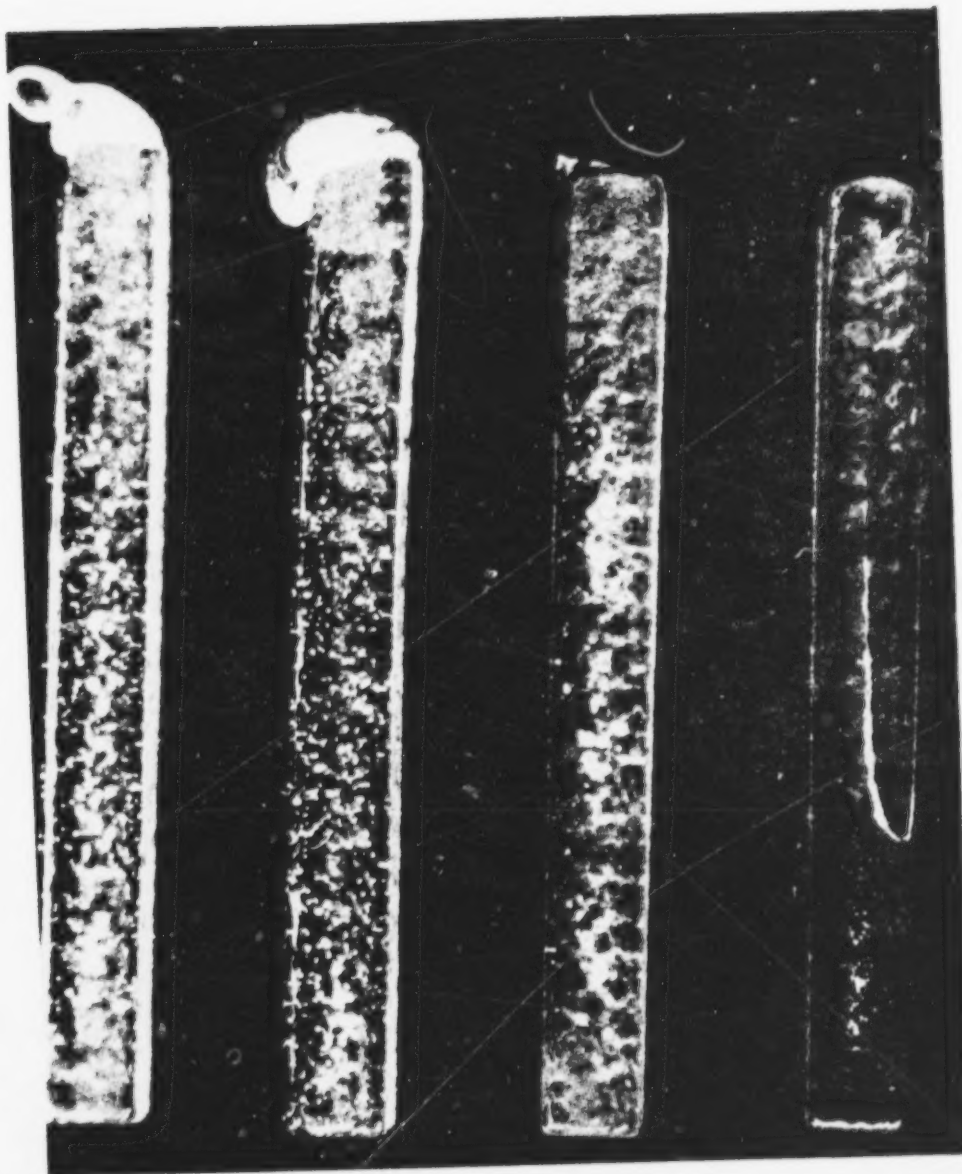


Figure 10. Photograph showing the effect of the addition of As_2O_3 , as a fining agent, on the incidence of bubbles in the test specimens (From top to bottom respectively, 0%, $\frac{1}{2}$ %, 1%, 2% As_2O_3).

TABLE II

COMPOSITION		ANNEALING TEMPERATURE °C
1.0 Na ₂ O · 1.0 SiO ₂		415
1.0	1.1	440
1.0	1.2	450
1.0	1.3	450
1.0	1.6	420

PRESENTATION AND DISCUSSION OF RESULTS

Since the strength of glass is not understood in the same detail as the strength of other brittle materials, it is very difficult to explain exactly what happens under every condition. The strength of glass is primarily controlled by flaws on the surface and secondarily those in the interior. It is this author's intent to first present his results and then give the explanation he feels the results show.

Composition Analysis

The first systematic investigation of the effect of composition on the strength of glass was that of Gehlhoff and Thomas (19) in 1926. Some (17) felt that it was almost impossible to draw convincing conclusions from their results, where others (1, 19, 20, 21, 23) have considered the effect of composition on strength.

The results of the present work on the effect of composition on the strength of glass is shown in Figure 11. It should be noted, that the results from Morey (1), and Gehlhoff and Thomas (23) are also depicted and the results from Morey's work with low Na_2O content is used. The points represented by the triangle are the averages, with the range given as a bar above and below the average. The results for the strength of the specimens from both the graphite mold and the steel mold are shown.

The rectangular specimens made in the steel mold had a smoother surface than those produced in the graphite mold. Thus, it seemed logical that those specimens would be stronger. However, upon testing,

BENDING STRENGTH (MOR), 1000 LBS/IN²

137

- GEHLHOFF AND THOMAS
- MOREY
- △ GRAPHITE MOLD
- STEEL MOLD
- | RANGE OF POINTS

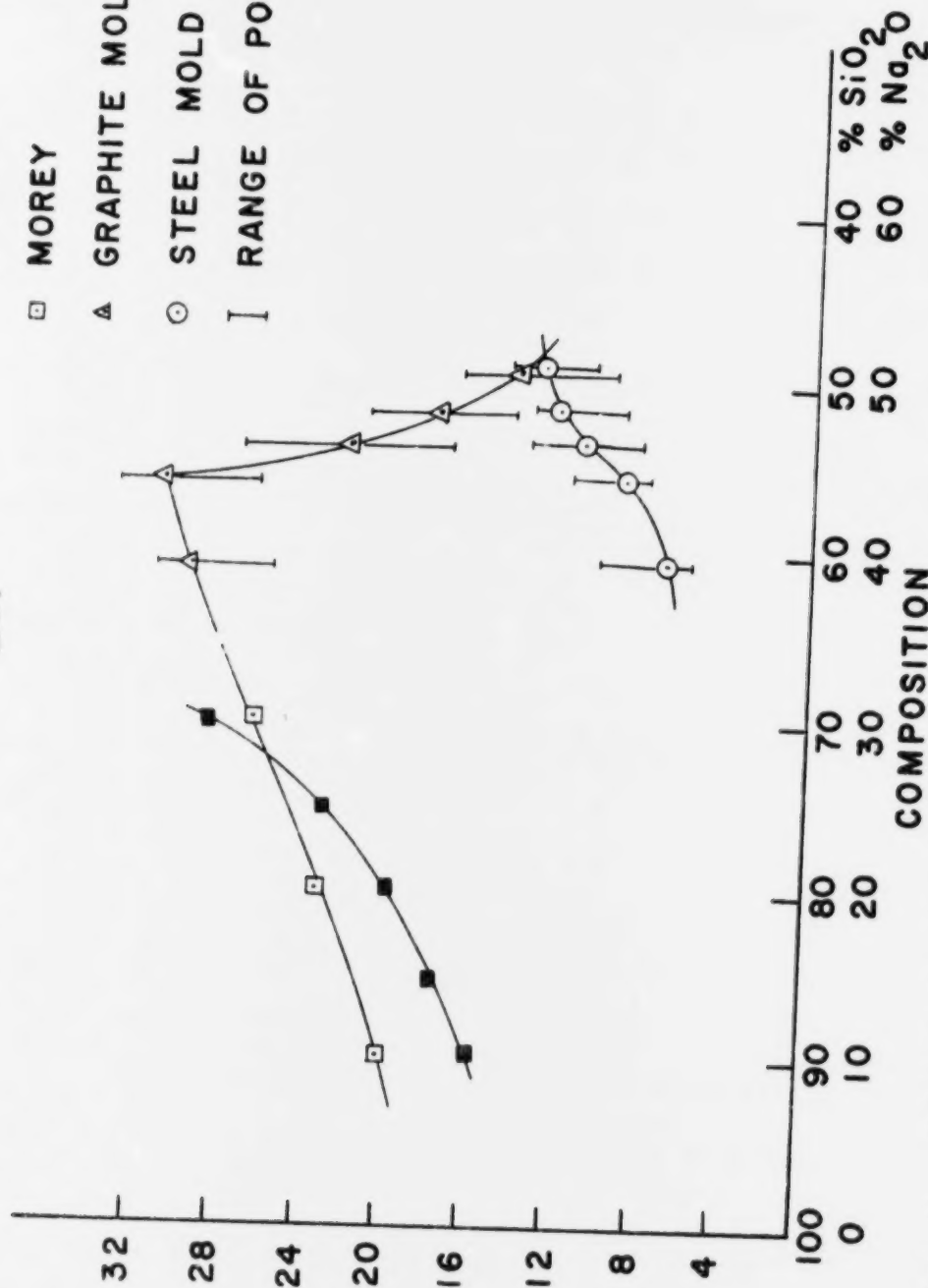


FIGURE 11. BENDING STRENGTH (MOR) VERSUS COMPOSITION

the specimen from the steel mold revealed much lower strengths than those from the graphite mold. This difference is also seen in Figure 11. Also, there was a distinct difference in the fracture patterns between the two types of specimens. Figure 12 shows the different fracture patterns. The difference in thermal conductivity between the steel mold and the graphite mold may have produced the differences in the strengths by altering the cooling rates for the specimens. This change in the cooling rate also led to the difference in fracture patterns. The leaching of iron or other substances from the steel mold may be another factor that influenced the surface of the specimens and reduced their strengths. These impurities would form complex glasses on the surface that could lead to a heterogeneity between the surface and interior glass.

The rapid decline of the strength of the specimen from the graphite mold with an additional increase in the Na_2O content past 44% is due to the saturation of the SiO_2 structure's interstices by sodium ions. Coupled with this fact, the Na_2O phase is becoming the primary crystalline phase, that is, the first phase to crystallize from the melt. These processes would produce large clusters of Na^+ ions or crystalline Na_2O that would disrupt the SiO_2 structure and reduce the strength. The compositions of higher silica contents fit the projected curve of the work by Morey.

The change in color with the change in composition was a noted visible change. The specimens of higher silica content, $1.0 \text{ Na}_2\text{O} \cdot 1.4 \text{ SiO}_2$ and above, possessed a clear and very transparent color. However, as the Na_2O content was increased, the presence of an aqua-bluish tint

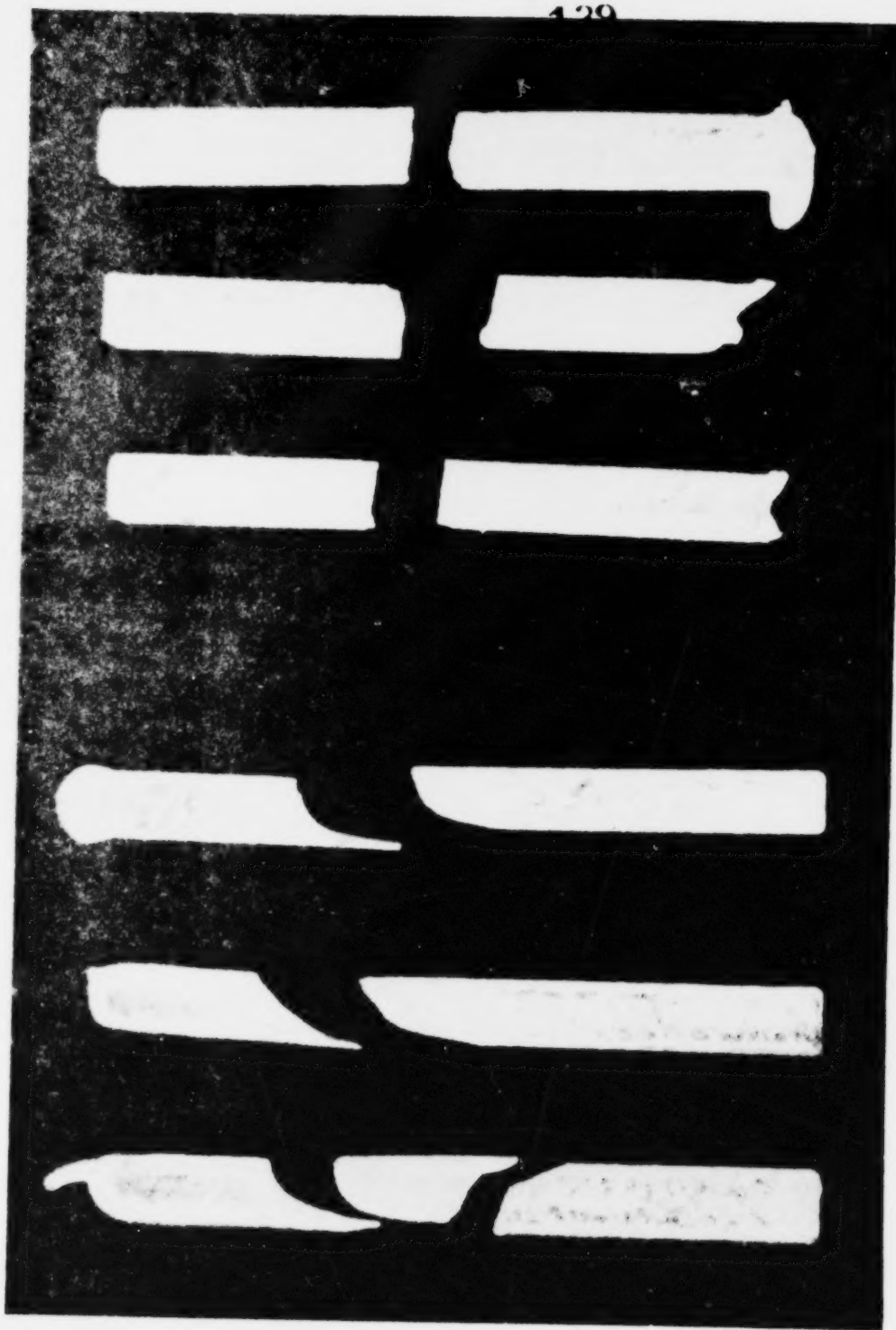


Figure 12. Photograph of the fracture patterns for the specimens from the two types of molds. The pattern representative of the steel mold is on the left, and the pattern representative of the graphite mold is on the right.

1.10

appeared and increased until the $1.0\text{Na}_2\text{O} \cdot 1.0\text{SiO}_2$ specimen became very blue-green. The change in the color could be from the presence of the sodium ion, other ions leached from the crucible by the higher Na^+ concentration, or a change in the valence state of the iron impurities.

Effect of Re-annealing

Since the specimens from the steel mold displayed significantly lower strength than specimens from the graphite mold, they were re-annealed to determine what effect this would have on their strengths. Figure 13 shows the results from reannealing over a 24 hour period. The composition used for this experiment was $1.0\text{Na}_2\text{O} \cdot 1.3\text{SiO}_2$ because concurrent studies indicate that this composition exhibits the dissolution kinetics required for adequate hydrolyzing. The relief of residual strains left from the first annealing period resulted with an increase in strength. However, after a period of nucleation, there is sufficient grain growth of Na_2O crystals to reduce the strength by disrupting the SiO_2 structure. Eventual complete devitrification would follow. This crystal growth would then decrease the strength as is shown after a re-annealing period of seven hours. This does not indicate that these specimens would require that length of time for annealing but indicates that more research should be done on mold materials and annealing schedules.

Prolonged Atmospheric Exposure

The $1.0\text{Na}_2\text{O} \cdot 1.3\text{SiO}_2$ composition was also used in this experiment. The specimens were periodically removed from a desiccator and exposed to the atmospheric conditions dictated by a dry bulb temperature of 77°F

PERCENT CHANGE IN BENDING STRENGTH

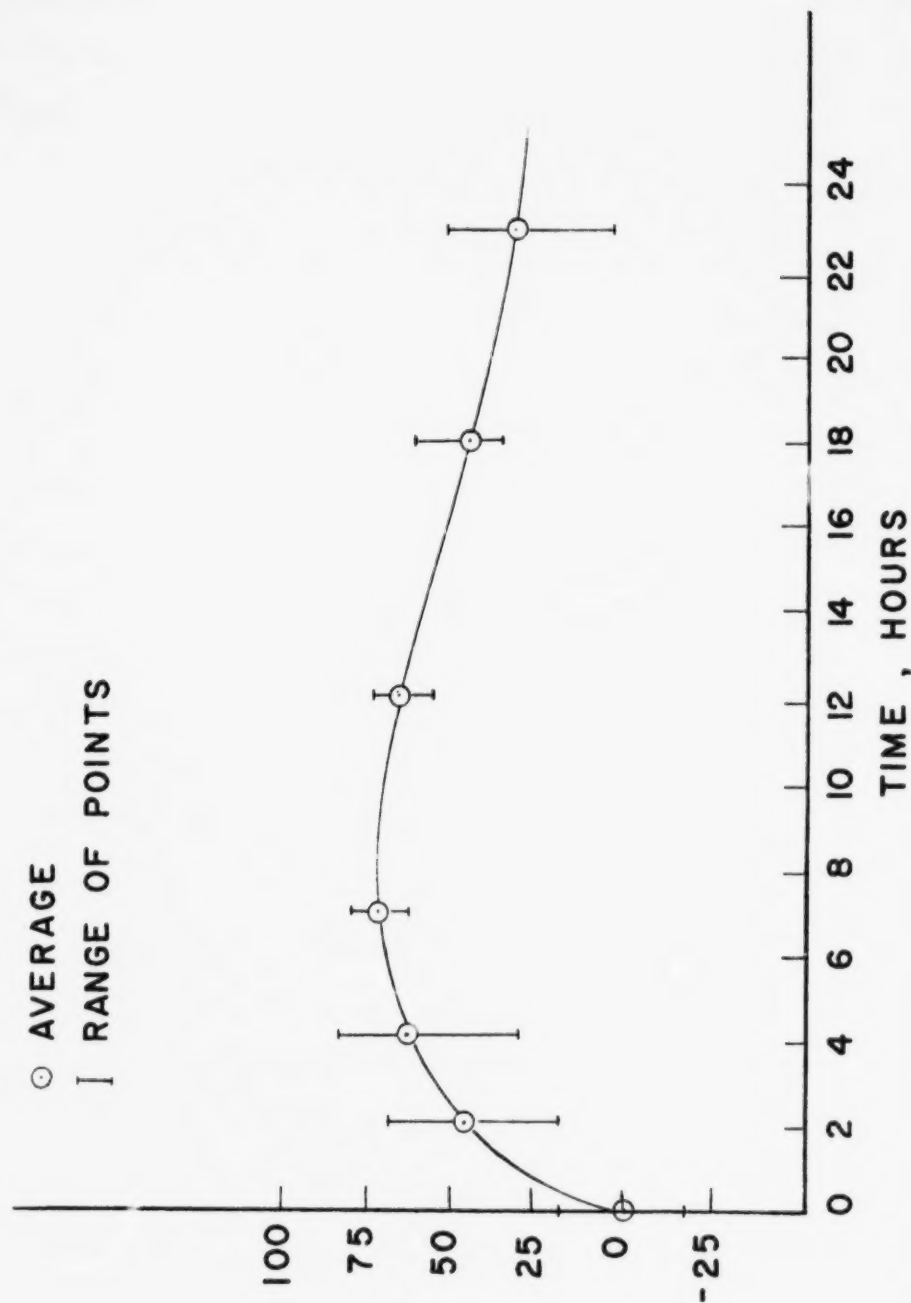


FIGURE 13. EFFECT OF RE-ANNEALING A $1.0\text{Na}_2\text{O} \cdot 1.3\text{SiO}_2$ COMPOSITION AT 450°C ON ITS BENDING STRENGTH.

and a wet bulb temperature of 71°F (relative humidity of 61%). Figure 14 shows the percent change in strength for the times indicated. Initial examination of this figure indicates a peculiar situation, a decrease and then an increase in strength.

These changes in strength can be explained through the examination of Figure 15, which shows the cross section of a specimen at four important time periods. The strength of glass is primarily surface dependent so the introduction of surface flaws decreases the strength by increasing the probability of propagating a crack through the sample. Figure 15A shows the unflawed surface of a molded sample. Figure 15B shows the flawed surface caused by abrasion from atmospheric dust and water attack. These additional flaws disrupt the surface and cause a decrease in the strength of the sample. As the silicate glass surface continues to absorb moisture and other atmospheric gases, it erodes these areas of higher energy, or flaws with small radii of curvature. This erosion, as seen in Figure 15C, forms a layer across the surface of the sample. The removal of these highly stressed flaws results in an increase in strength. Applying the Griffith Flaw Theory to the conditions present in Figures 15B and 15C, the actual stress concentration at a crack tip can be expressed by:

$$\sigma_m = 2\sigma\sqrt{\frac{c}{\rho}}$$

and

σ_m = actual stress for failure

σ = theoretical stress for failure

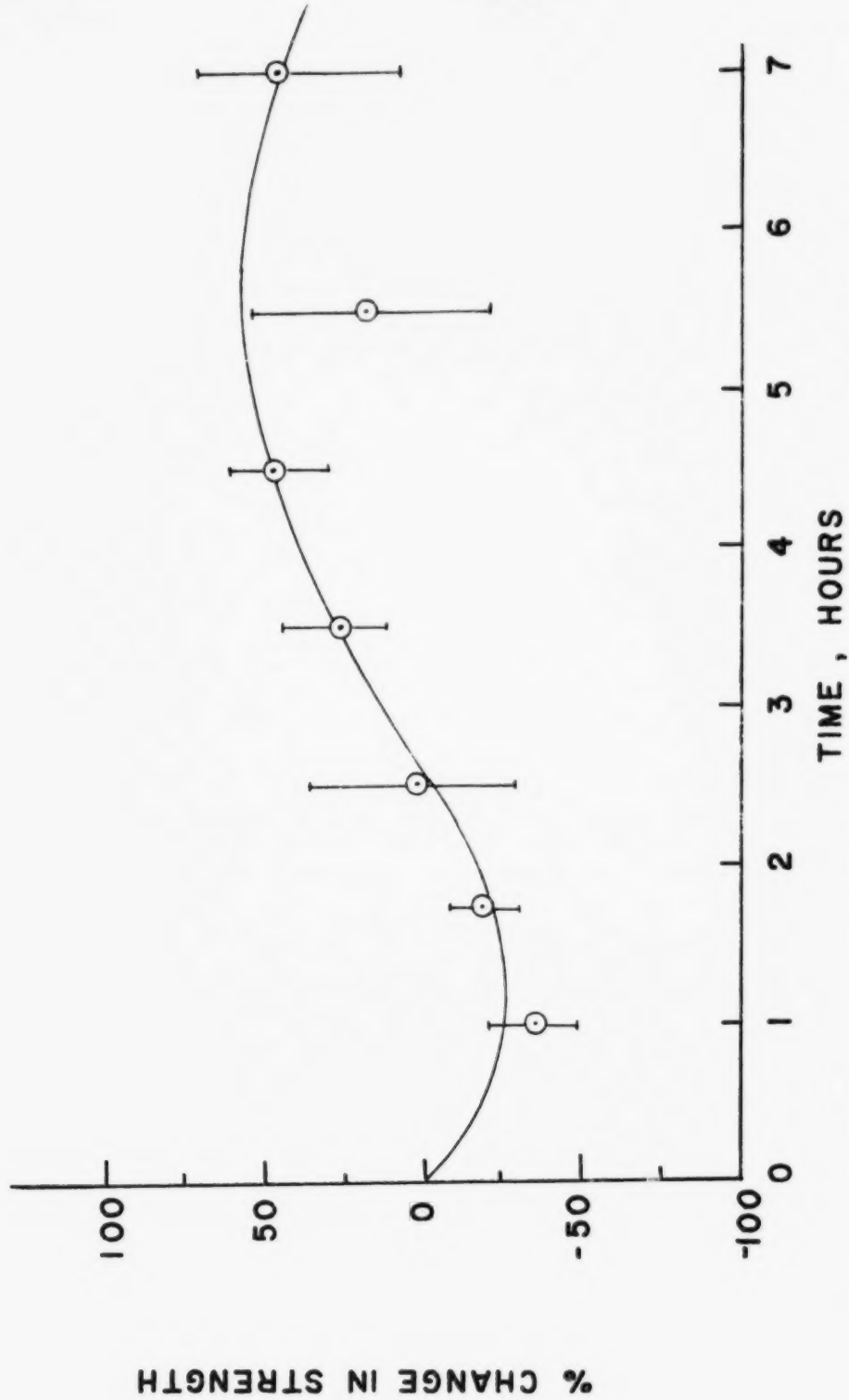


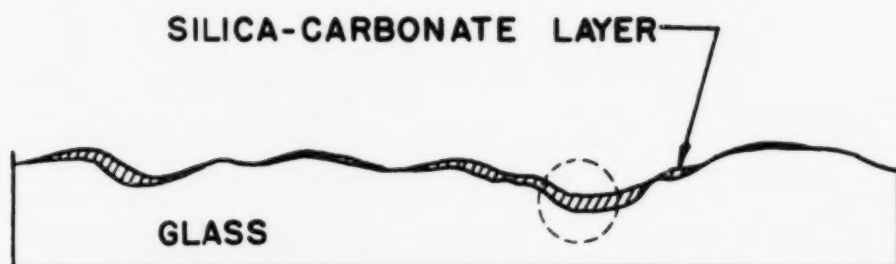
FIGURE 14. PERCENT CHANGE IN STRENGTH VS THE TIME OF ATMOSPHERIC EXPOSURE



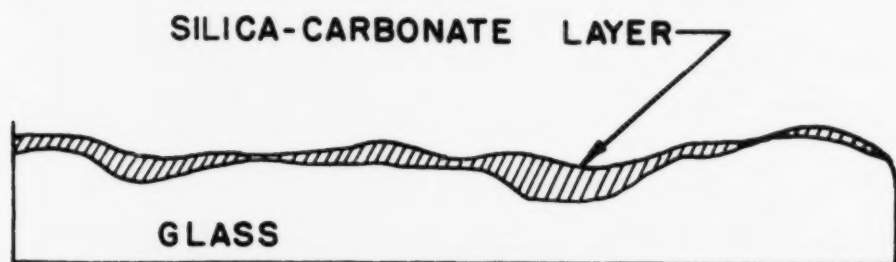
A. SURFACE AS FORMED



B. SURFACE AFTER BEING FLAWED



C. SURFACE AFTER SHORT EXPOSURE



D. SURFACE AFTER PROLONGED EXPOSURE

FIGURE 15. ILLUSTRATION OF HOW SURFACE FLAWS ARE ELIMINATED AFTER PROLONGED EXPOSURE TO THE ATMOSPHERE

c = one half the axis length of the crack

ρ = radius of curvature of the crack tip

it can be shown that as the radius of curvature of the crack tip increases the strength increases by decreasing the probability of propagating the crack through the specimen. When there is sufficient erosion of the glass to produce a reduction in the cross sectional area as illustrated in Figure 15D, there is a reduction in the overall strength.

The surfaces shown in Figure 16 support the author's theory on the change in strength. As seen in this series of pictures, the layer grows across the surface until it completely covers the surface. This completion occurs between four to five hours and coincides with the leveling off and decline of the curve shown in Figure 14.

The author is not in a position to say of what this surface layer is composed. However, Phillips (21) says that sodium silicate is leached from the glass and undergoes hydrolysis so that the layer contains sodium hydroxide and colloidal silicic acid. In the presence of carbon dioxide a further reaction occurs between this gas and the alkali, resulting in the formation of sodium carbonate and a surface layer of finely divided silica.

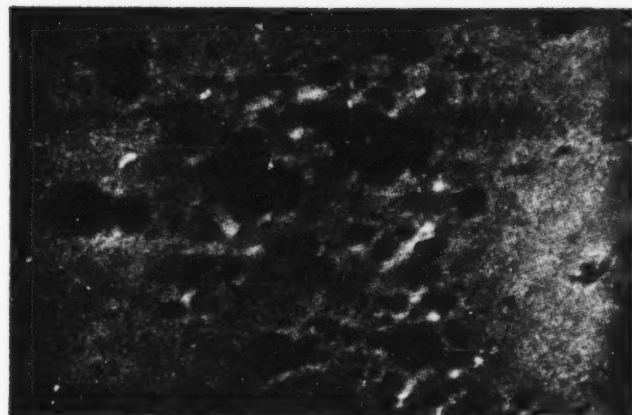
Coating Evaluation

There are three types of coatings under investigation for use as a moisture barrier. Organic epoxies, ion exchanged surfaces, and a chemical deposited surface are under simultaneous study. It is impossible to conclusively evaluate their effect on strength at this time.

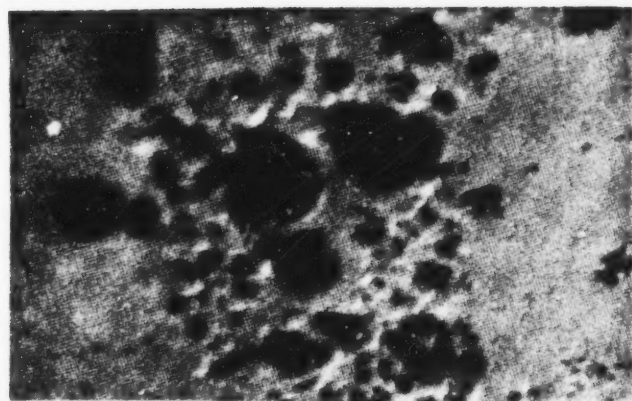
The only coating available for testing was the organic epoxy. This was applied to a heated specimen (200°C) by passing the specimen through



C. 90 Minutes



B. 60 Minutes



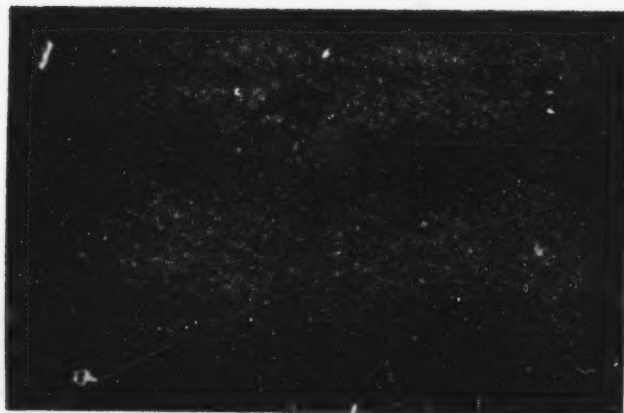
A. 30 Minutes

Figure 16. This series of photographs shows the absorption of moisture by the surface of a $1.0\text{Na}_2\text{O} \cdot 1.2\text{SiO}_2$ glass and the growth of the resulting layer across the surface (2000X).

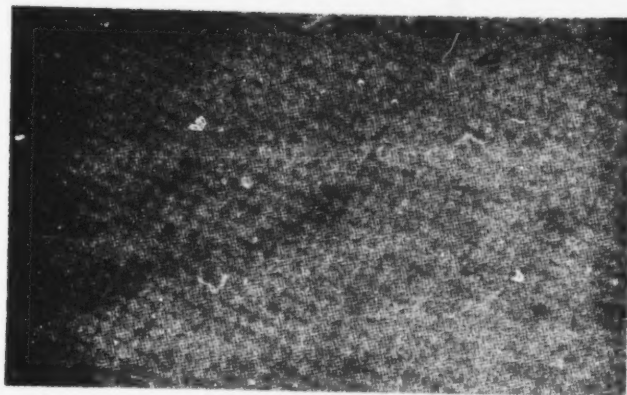
117



D. 120 Minutes



E. 180 Minutes



F. 240 Minutes

Figure 16. Con't.

a fluidized bed of the powdered resin. Upon cooling, the specimens were placed in a desiccator and stored until testing. As in the other tests, the $1.0\text{Na}_2\text{O} \cdot 1.3\text{SiO}_2$ composition was used. The results of testing yielded a decrease in strength by approximately 12%. This is a very incomplete experiment at this time; however, continuation of present work should yield more pertinent information concerning coatings.

CONCLUSIONS

1. The glass compositions from the $1.0\text{Na}_2\text{O} \cdot 1.3\text{SiO}_2$ to the $1.0\text{Na}_2\text{O} \cdot 1.6\text{SiO}_2$ range seem to possess sufficient strength and ease of workability to be used as a container material. However, no decision for the selection of a definite composition can be made until all system parameters are evaluated.
2. The technique of molding glass test specimens is not the optimum procedure for producing samples because it is too time consuming. Another method, like pulling glass rods, should be developed to mass produce specimens.
3. The formation of the silica-carbonate layer on the surface of the glass after prolonged exposure indicates that some type of atmospheric control will be necessary during the production process.
4. The change in strength between the specimens from the two types of mold indicates that more research into mold materials is needed.
5. The change in strength of the specimen formed in the steel mold, after a period of reannealing, indicates that an optimum period of annealing exists and continued research in this area is needed.
6. The addition of 2% by weight of As_2O_3 is needed as a bubble release agent to sweep the melts of bubbles prior to molding.

CONTINUATION OF RESEARCH

At present there are corollary studies being pursued in the areas of glass dissolution kinetics, organic coatings, ion exchanged surfaces, and a continuation of the work on chemical vapor deposition (25). All these areas will influence the composition selection and determine the feasibility of this project.

This work has answered but a few of the questions concerning the feasibility of using a sodium silicate glass as a water soluble container. However, it has been a guide in determining what paths will be followed in future research. The molding of glass specimens is not the optimum method for producing test samples. This author suggests that the mass production of uniform samples by a pulling technique, similar to the one used by Watanbe and associates (26), be given serious consideration as a faster and more efficient method.

The work on dissolution kinetics is vitally important in selecting the desired composition. This is very time consuming work that encounters many obstacles. But, after the results are analyzed, that work will combine with this work on mechanical strength to yield the selection of a composition that possesses sufficient mechanical strength and adequate solubility. Also important is the coating that acts as a vapor barrier to protect the glass surface. This coating must resist chipping or scratching from handling, and yet be feasibly applied and reasonable in cost. These components must all function as an integral system before success is achieved.

This work has justified the continuation of research on this project, while indicating that additional work is needed on mechanical properties and new research should be investigated on viscosity and other properties that will be of vital importance to the glass manufacturing industry.

1. Morey, G. W., The Properties of Glass, Reinhold Publishing Corp., New York, (1954).
2. Anonymous, "Why the U.S. Is In Danger of Being Engulfed by its Trash," U.S. News and World Report, Washington, D. C., (September 8, 1969).
3. President's Science Advisory Committee's Report of the Environmental Pollution Panel, "Restoring the Quality of Our Environment," Washington, D. C., 141, (November, 1965).
4. Glass Industry, 92(1):40, (1968).
5. Anonymous, "Solid Waste Handling in Metropolitan Areas," U. S. Department of Health, Education, and Welfare, Washington, D. C., (February, 1964).
6. Anonymous, "Proceedings--The Surgeon General's Conference on Solid Waste Management," U.S. Department of Health, Education, and Welfare, Washington, D. C., (July, 1967).
7. Anonymous, "Proceedings of the National Conference on Solid Waste Research," American Public Works Association, (1963).
8. "Research and Training Grants," U.S. Department of Health, Education, and Welfare, Washington, D. C., (1968).
9. Vail, J. G., Soluble Silicates: Their Properties and Uses, Vol. 11, Reinhold Publishing Corp., New York, (1952).
10. Rawson, H., Inorganic Glass Forming Systems, Academic Press, New York, (1967).
11. Moore, H., and Carey, M., "Limiting Composition of Binary Glasses of the Type $xR_{2O} \cdot SiO_2$ in Relation to Glass Structure," Journal of the Society of Glass Technology, 35:43-57, (1951).
12. Imaoka, M., and Yamazaki, T., "Survey of Glass-Forming Regions in Simple Silicates," Journal of the Ceramic Association of Japan, 61:13-14, (1963).
13. Scholes, S. R., Modern Glass Practices, Industrial Publications, Inc., Chicago, (1951).
14. Samseons, M. O., Journal of the Society of Glass Technology, 182, 517 (1926).
15. Pranatis, A. L., "Coaxing Effect Furing the Dynamic Fatigue of Glass," Journal of the American Ceramic Society, Vol. 52 (6), 340-341 (1968).
16. Holland, A. J. and Turner, W. E. S., Journal of the Society of Glass Technology, 20, 72 (1936).

17. 1969 Book of ASTM Standards, Part 13, Refractories, Glass and Other Ceramic Materials, Published by the American Ceramic Society for Testing and Materials, Philadelphia, Pa., (1969)
18. Anonymous, "Glass Strength Test," Glass Industry, 45(2), 80-81, (1964).
19. Guyer, E. M., "Mechanical Properties of Some Rolled and Polished Glass," Journal of the American Ceramic Society, J13:624, (1930).
20. Williams, A. E., "The Mechanical Strength of Glazing Glass," Journal of the American Ceramic Society, J6:980, (1923).
21. Phillips, C. J., Glass: The Miracle Maker, Pitman Publishing Corp., New York, (1941).
22. Rudnick, A., Hinter, A. R., and Holden, F. C., "An Analysis of the Diametral-Compression Test," Materials Research and Standards, Vol. 3:4, 283-289, (April, 1963).
23. Gehlhoff, G., and Thomas, M., "An Investigation of the Effect of Composition on the Strength of Sodium Silicate Glass," Zeitschrift Fver. Physik., 7:105, (1926).
24. Kingery, W. D., Introduction to Ceramics, Wiley Publishing Co., New York, (1960).
25. Cooper, M. M., "Protective Oxide Coatings for Glasses by Chemical Vapor Deposition," Progress Report No. 1 submitted to United States Public Health Service under Research Grant No. UI00651, (April, 1961).
26. Watanabe, M., Caporali, R. V., and Mould, R. E., "The Effect of Chemical Composition on the Strength and Static Fatigue of Soda-lime Glass," Physics and Chemistry of Glasses, Vol. 2, No. 1, (February, 1961).

TABULAR RESULTS OF VARIOUS TESTS

Although the graphical results are displayed during the text of the thesis, this section was added to clarify any questions concerning the number of specimens tested yielding usable data, numerical averages, and standard deviations for each experiment.

TEST	COMPOSITION	NO. SPECIMENS TESTED	NUMERICAL AVERAGE	STANDARD DEVIATION
Bending Strength	1.0 Na ₂ O · 1.6 SiO ₂	11	29,320	2,390
Versus Composi-	1.0 Na ₂ O · 1.3 SiO ₂	18	30,850	1,810
tion using	1.0 Na ₂ O · 1.2 SiO ₂	9	22,010	2,520
graphite mold.	1.0 Na ₂ O · 1.1 SiO ₂	10	17,870	2,670
	1.0 Na ₂ O · 1.0 SiO ₂	7	13,990	1,900
Bending Strength	1.0 Na ₂ O · 1.6 SiO ₂	12	6,880	1,470
Versus Composi-	1.0 Na ₂ O · 1.3 SiO ₂	23	8,750	970
tion using steel	1.0 Na ₂ O · 1.2 SiO ₂	19	10,960	1,620
mold.	1.0 Na ₂ O · 1.1 SiO ₂	11	12,030	1,270
	1.0 Na ₂ O · 1.0 SiO ₂	8	12,790	1,080
Effect of Re-	1.0 Na ₂ O · 1.3 SiO ₂	23 at 0 hr	13,980	760
annealing on		6 at 2 hr	11,930	1,860
Bending		5 at 4 hr	13,270	2,010
Strength.		6 at 7 hr	13,980	870
		4 at 12 hr	13,650	1,170
		5 at 18 hr	11,800	1,170
		4 at 23 hr	10,910	1,840

TEST	COMPOSITION	NO. SPECIMENS TESTED	NUMERICAL AVERAGE	STANDARD DEVIATION
Effect of pro- longed Exposure to the Atmosphere	1.0 Na ₂ O · 1.3 SiO ₂	23 at 0 hr	8,750	970
		4 at 1 hr	5,510	690
		6 at 1 3/4 hr	6,810	560
		5 at 2 1/2 hr	9,180	1,490
		5 at 3 1/2 hr	11,370	860
		4 at 4 1/2 hr	12,680	1,370
		3 at 5 1/2 hr	10,500	2,340
		5 at 7 hr	12,650	1,750

PART III

THE RATE OF DISSOLUTION OF SODIUM SILICATE GLASSES IN AQUEOUS SOLUTION

The rate of reaction of soluble silicate glasses with aqueous solutions was studied. The work reported is part of an investigation into the feasibility of processing glass containers after use so that one large source of solid waste can be relieved and possibly eliminated.

The apparatus used in studying the rate of reaction of the glasses with water is described in detail. Two basic methods of rate determination are discussed. These two methods are measurement of the sodium ion concentration in solution, and continuous measurement of the total bulk weight loss. These two parameters are plotted versus time and related to the rate of reaction of the glasses with the water.

The glasses studied were simple sodium silicate glasses in the range $1.0 \text{ Na}_2\text{O} \cdot 1.0 \text{ SiO}_2$ to $1.0 \text{ Na}_2\text{O} \cdot 21. \text{ SiO}_2$. The glass batches were melted at 2050°F and annealed at 800°F . Surface characteristics of samples were difficult to control, but were generally uniform. These samples were dissolved, and the rates of reactions with water under various experimental conditions were plotted. Particular emphasis was placed on the variables affecting the rates of reaction. The variables observed were the effects of time, temperature, volume of solvent, and turbulence.

The rates of dissolution were found to increase with temperature and turbulence. The effect of the volume of solvent to which the glass is exposed was less than expected.

It was found that glasses of a rapid dissolving sodium silicate composition dissolved as a simple solution process in the same manner as a sugar crystal. In more durable glasses, there is the formation of a boundary layer through which sodium ions and water molecules must diffuse for solution to occur.

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INTRODUCTION

In a society which has its share of problems such as air and water pollution, conservation of natural resources, and deterioration of the cities, there now is another problem which must be met and solved if Americans are to go on enjoying their present standard of living. The problem is called "solid waste management."

Solid waste management is not a new problem, but it is odd that many people do not realize that it even is a problem today. If a person happens to live near a city dump, he may be quite aware of the problem, for it strikes home on two sides. He finds that his property value is not what it might otherwise be and also the environment may be poor due to air pollution or the unsightly dump.

However, most people go about their daily lives never giving thought to what the "garbage man" does with their solid waste. All they ask is that it be carted off regularly. In general, the public has been apathetic until their trash cans stay full for an extra day.

The amount of solid waste produced in a country is closely correlated to the standard of living of the people. All prognosticators are pointing to a boom in the 1970's for the United States economy. As bad as our solid waste problems are today, every indication is that they are going to become much greater, unless some positive steps are taken immediately. Government has already recognized the problems and started to move to aid in solving them in numerous ways. It still

remains for the public and industry to become as concerned as they should be about the magnitude of the problem. Municipalities and industry need a public mandate to get together and try to alleviate the problem.

The importance of convenience to the consumer has now become firmly established as a guiding principle in the design of a packaging material. With this in mind, beverage container manufacturers are going more and more to the disposable bottle. The Midwest Research Institute has projected that between 1966 and 1976 the number of beverage containers in use in the United States will double to an estimated 62.9 billion units (1). In this period the use of cans and non-returnable bottles will also double. The problem is: what do we do with these wastes?!

It should be realized that it is going to be necessary to deal with this problem on a long term basis. At the local level, sanitary landfills are the primary method of disposal. However, this is only a temporary means of disposal which holds a remarkable similarity to the housewife sweeping the dust under the carpet. It may be put out of sight temporarily, but it is still there. This all points to one of the basic problems concerning sanitary landfills. This problem is the settling rate which occurs when raw refuse is used. "Compaction of the various packaging and other materials generally is not complete, creating undesirable voids which trap liquids and gases. Along with decaying organic matter, this commonly results in noticeable settling of the landfill for perhaps 15 to 25 years even in a properly operated landfill" (2).

Perhaps the answer to the problem lies in taking a different approach. Instead of trying to devise cheap methods of disposal as is the general practice today, it may prove beneficial to work on means of attaining long-range results even if they prove more costly than the short-range operations.

It is this approach that is being taken at Clemson University. Work is being done to perfect a one-way container, made of water-soluble glass, which when discarded can be broken and dissolved. While in use the container must be covered by a protective coating both inside and out to prevent any degradation. Later this coating can be broken and the bottle can be dissolved.

This research, supported by a Solid Wastes Program grant, could aid in the waste disposal problems resulting from the increasing use of nonreturnable glass containers. It is estimated that 26 billion of these containers are discarded each year in the United States (2). The objective of this research was to give insight into the factors affecting the dissolution of sodium silicate glasses. The variables which were studied were the effects of composition, temperature, exposure time to solvent, turbulent conditions in the system, and sodium concentration in the solution. The data collected was used to determine the mechanisms which control the solution process.

These results give criteria as to what type of glass is more suitable for implementation on a practical basis in the glass industry as a water-soluble glass container. It also serves as a guide for the avenues of approach which would prove most beneficial to future researchers in this area.

LITERATURE SURVEY

There has been a substantial amount of work done in the area of the reaction of glass with aqueous solutions, or the chemical durability of glasses.

Silvermann (3) lists some general factors to consider in the chemical durability of any glass. These factors are:

- (1) State of division: The amount of surface exposed by a body determines how fast it reacts.
- (2) Condition of the glass surface: If the glass surface is continuous, the effect will be different than if the surface has been chipped, scratched, or abraded.
- (3) Time of exposure to the solvent: Exposure time may determine the extent of external or internal influence on stability.
- (4) Temperature: Conditions during firing and after fabrication affect durability.
- (5) Pressure: External pressure during treatment or use and internal pressure of contents or strain may affect stability.
- (6) Concentration of extraneous reactants
- (7) Radiation
- (8) Mold and Bacteria
- (9) Composition

F. R. v Bichowsky (4) has presented six mechanisms or steps which take place theoretically at some time during the "weathering" of

glass in an aqueous environment. These mechanisms are:

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- (1) Adsorption of water on the surface
- (2) Diffusion of adsorbed water molecules into the body of the glass
- (3) Reaction of the dissolved and adsorbed water with the glass, forming a surface film of a character depending on the glass composition
- (4) Soaking up of water by this film thereby getting more reaction
- (5) Extraction of soluble salts from this surface film
- (6) Solution of the silica skeleton film in the strongly alkaline solution formed.

It has been shown that the extent to which any glass may be attacked or partially dissolved by water is greatly dependent upon its composition. Sodium disilicate has long been melted for the manufacture of water glass. This composition is used because it is water soluble. Sodium metasilicate glasses dissolve even more rapidly. Whenever metallic oxides are introduced, insoluble silicates are formed which decrease the rate of solution. This rate is also affected by other factors such as water impurities, striations in the glass in which the ratio of alkali to silica varies from the main composition of the glass, and strain which is set up by cooling through an uncontrolled temperature cycle. Of course such physical things as amount of exposed surface area and the degree of circulation of the liquid will affect the rate of solution (5).

Morey (6) and Scholes (7) are of the opinion that it is incorrect to speak of the solubility of glass as one would discuss the solubility of salt. The action according to them is one of diffusion and disintegration and not one of true solution. All that can be measured and compared is the rate of attack of the solution on the glass, not the solubility of the glass in that medium. The problem arises because the glass changes its internal composition. "The mechanism of the attack of water upon an ordinary glass cannot be accurately set forth in the present state of the knowledge. But it is highly selective" (7).

When silicate glass is exposed to water, there is the transport of water constituents into the glass. The reaction which follows is dependent upon the composition of the glass and the capacity of the water to act as a sink for metal hydroxides (8). There are two types of general attack to be considered: attack on non-bridging oxygen atoms by reagents with an electron deficit and attack on the network silicon atoms by reagents with electron excess. Acids and neutral solutions are called electrophilic reagents. They attack positions with excess electrons. This type of attack is typified by a form of ion exchange between the glass and attacking solution (9). When in contact with a liquid aqueous phases, glasses which contain alkali cations will undergo an ion exchange mechanism in which the liquid water acts as a sink for alkali hydroxide by dissolving them (8).

Alkalines are nucleophilic reagents. They attack positions with a deficit of electrons. Alkaline attack is usually typified by degradation of the glass network.

Water is a very good solvent of glass because it can attack the glass both electrophilically and nucleophilically. Water ionizes to form H^+ ions which are electrophilic and OH^- ions which are nucleophilic. Even a neutral water molecule can be weakly nucleophilic (9).

In an ordinary commercial glass, Scholes (6) says that sodium silicate is leached from the glass and undergoes hydrolysis. The solution which is formed contains sodium hydroxide and colloidal silicic acid. The sodium hydroxide which is produced on the surface reacts with carbon dioxide in the air while the silica separates out. The surface film then becomes a deposit of crystals of sodium carbonate together with finely divided silica. If the attack has not proceeded too far, the film can be washed off by a dilute acid or even by water, but if attack is severe, the surface is permanently ruined. The relative insolubility of silica causes it to exert a protective action which causes the attack to proceed more slowly as time goes on.

Most literature concerns itself with solving the problem of making a glass which is less susceptible to attack by aqueous solutions. Therefore, it is necessary to use the information obtainable in reverse to get a soluble glass. The literature is also of some assistance in specimen preparation in the laboratory.

It has been shown that the range of glass formation in the Na_2O-SiO_2 system is continuous from SiO_2 to a limiting composition close to that of the metasilicate Na_2O-SiO_2 . The limiting composition depends on the experimental conditions. The Na_2O content of the glass can be increased as the melt becomes smaller and the cooling rate be-

comes greater. Imaoka and Yamazaki found it possible to make glasses containing up to 57.8 mole per cent Na_2O on a scale of 1-2 grams. It is essential that in all work the melting and cooling conditions be reported when talking about the region of glass formation in a system.

The limit to glass forming compositions in the $\text{Na}_2\text{O}-\text{SiO}_2$ system coincides almost exactly with the composition at which Na_2O becomes the primary crystalline phase or the first phase to crystallize from the melt. At this composition, sodium begins to crystallize before the glass crystallization can be stabilized. This change will be reflected in the kinetics of the process (10).

The composition will have a pronounced effect on the rate of devitrification. Dietzel and Wickert (11) studied this effect by making measurements on twenty compositions in the $\text{Na}_2\text{O}-\text{SiO}_2$ system containing 0-42 mole per cent Na_2O . "The stability decreases markedly in the range 0 to 0.5 mole per cent Na_2O . Then in the range above 10 mole per cent Na_2O , it increases to a maximum at 23 mole per cent Na_2O , a composition close to the eutectic between silica and sodium disilicate, $\text{Na}_2\text{Si}_2\text{O}_5$ " (10). The explanation for this type of curve is that the stability will decrease as more Na_2O is introduced because the extra non-bridging oxygens will break down the continuity of the silica network. Low stability at those compositions corresponding to the compounds Na_2SiO_5 and Na_2SiO_3 occurs because there is a close similarity between the structure of the melt and that of the corresponding crystal. This condition enables crystallization to occur readily (10).

Bowen (12) acknowledges the problems associated with obtaining the proper annealing temperature for a glass. It is necessary to anneal the glass to free it from excessive strain. This strain can have a marked effect on the internal properties of the glass and its chemical susceptibility to hygroscopic attack. The choice of temperature is quite important. To be able to choose the proper annealing temperature, it is necessary to know the crystallizing power for various temperatures of the glass to be annealed, in order to choose a temperature that will not induce devitrification. Both annealing and devitrification will take place faster at higher temperatures. In the same manner, lowering the temperature may not help because there is no definite lower limit of devitrification temperatures and the rate of annealing may be too slow if the temperature is too low. Compositional changes, of course, can be made which will affect the annealing rate or decrease the rate of devitrification. Cox (13) points out that those glasses higher in soda, low in barium, and high in silica, tended most readily to devitrification. Little devitrification was noticed in glass high in potash content, if arsenic was not present.

There are many literature sources which relate methods of increasing durability of a glass. It is known that solubility and the tendency to weather are increased directly as the lime to soda ratio in a glass (14). Baillie (15) and Vail (5) both point out that a glass becomes less durable as the simple silicate content is increased. It has been shown that there is better chemical durability for soda glasses than for potash glasses made up to the same molecular

formula, However, a glass composed of both alkalies is more durable than one containing either Na_2O or K_2O alone (6). Sen and Tooley (16) state that the maximum durability of a glass composed of simple K_2O and Na_2O is at a $\text{K}_2\text{O}/\text{Na}_2\text{O}$ ratio of 2.6/1.0 by weight.

It is widely known that the presence of alumina in the glass will retard the weathering of the glass. The addition of 1.5 to 2.5% alumina to the glass composition will improve the chemical durability significantly. The greatest benefit will occur when the alumina is one-eighth the soda content (17).

The reaction product of the proper quantities of sodium carbonate and silica will be a clear glass of two types. One type is neutral glass, Na_2O to SiO_2 ratio of 1/3.3. It is pale bluish or greenish in color. The other type is alkaline glass, ratio of 1/2.1, and its color is usually yellowish (5).

Niggli (18) studied the reaction of sodium carbonate and silica at 898° - 956° Centigrade and one atmosphere carbon dioxide. All CO_2 was expelled and equilibrium could be approached from both directions. It was also found that the amount of CO_2 displaced per mole of silica was greater the smaller the amount of silica in the melt.

Howarth, et al (19), studied the reaction from equimolar to a composition of 4 silica:1 soda. The equimolar mixture took 40 hours for complete expulsion of the CO_2 at 700°C . At temperatures above 900°C , the speed of reaction in all the mixtures increased rapidly. Commercial soluble silicate glasses are for reasons of economy made at temperatures in the range of 1200 to 1400°C . Preliminary heating

at about 700°C allows most of the carbon dioxide to escape. Niggli found that it takes a ratio more siliceous than 1 alkaline oxide to 2 SiO₂ to expel all of the CO₂ from glasses at 900 to 1000°C (5).

There have been many attempts made at measuring the durability or weathering or rate of attack of a glass by its environment. Morey is quite skeptical of any such results which may be obtained by the numerous methods now in use and probably justifiably so. The required precise control of experimental conditions is one reason for such skepticism. The tests used in the past range from visual classification of "not affected" and "very affected" to some very precise and elaborate titration measurements recommended by the Committee on the Chemical Durability of Glass of the American Ceramic Society. All have some common points of agreement and some differences. All recognize the importance of controlling surface area; of attaining homogeneity in the glass; and of controlling external factors such as temperature, exposure time, and concentration of solution. The basic differences lie in the method of determining how much deterioration has taken place. One school of thought maintains that the best method is the direct method of weighing both before and after exposure. The other way is to measure the amount of attack by measuring the quantity of alkali yielded to the solvent under definite conditions. This has been done by the use of flame photometry, by measuring electrical conductivities, and by using elaborate titration techniques. Morey is quick to bring attention to the fact that any comparison of the results of one observer with those of another is rarely possible,

and in any case the validity of any such comparison requires proof.

Morey dealt with systems of wide ranges of temperatures and pressures and decided that true phase equilibria do not exist in systems involving water and complex silicate minerals. When performing an experiment on the reaction of a glass with aqueous solutions, several mechanisms may be involved in any experiment. The rate-controlling processes may vary during the experiment as well as with time and temperature, with the ratio of glass surface area to the volume of solution, and particularly to the way the pH⁺ of the solution is controlled. The basic objective of an experiment in this area is to control the time and temperature of the experiment adequately and exercise control over the compositional change of the attacking medium (20).

Douglas and Isard (21) suggest that the process of dissolving a soda-lime-silica glass is diffusion controlled. A model has been developed in which the rate controlling process is the diffusion of Na⁺ through the glass to the surface in order to react. This work found in general a linear relation of the quantity of alkali extracted from the glass to the square root of time in the early stages of the reaction. In later stages it was found that the quantity of alkali was linearly dependent on time.

In later work, Rana and Douglas (22) found also that the rate of reaction varies to a close approximation $\sqrt{t}$ in the early stages, but later the rate of reaction becomes constant. It was also found that in binary silicate glasses the ratio of silica to alkali removed

during the reaction is much less than the ratio of the constituents in the glass. It was shown that the change in dependence of the rate of reaction from $\sqrt{t}$ to linearity takes place in a short time interval. This "time of changeover" varies from glass to glass and from temperature to temperature. The amount of alkali removed is approximately constant up to the changeover.

Haller (8) proposes that "water uptake follows initially a parabolic law and is accompanied by a volume expansion. The rate of uptake is affected by the previous hydration history of the samples, suggesting that an irreversible change of the glass structure is associated with the diffusion of the water into the glass." The model proposed by Douglas and El Shamy (20) suggested that a leached layer is formed on the surface of the glass. Silica is then dissolved at the leached layer-water interface while sodium ions diffuse across the leached layer from the glass into the water. The change in rate from root time dependence to linear reflects that as time passes diffusion will slow as the leached layer becomes thicker.

The rate of extraction of alkali from the glass is independent of pH^+ when it lies between 1 and 9. If the pH^+ is greater than 9, the rate of extraction decreases with increasing pH^+ . The effect on silica extraction is opposite. The rate of extraction increases with increasing pH^+ . It was found that pure water below 100°C does little compared to alkaline solutions. There is a strong influence of alkali level on the rate of silica attack. This work served to confirm Morey's deduction that the action of water on glass is a com-

plicated decomposition reaction and not a normal solution process. This is shown by the occurrence in solution of species chemically different from the original glass which implies some rearrangement of chemical bond occurs. It was also shown that alkali ions are, always, extracted in excess of the silica. This leaves an alkali-deficient leached layer which is not appreciably different in volume from the original glass. At the boundary between the leached layer and the solution, there are sites available to cations. It was surmised that the diffusion process must be a flow of hydrogen ions from the solution and an equivalent flow of sodium ions from the glass into the solution. It is believed that a glass of low chemical durability would have a large leached layer-solution zone and a smaller leached layer-glass zone (20).

EXPERIMENTAL PROCEDURE

The glasses studied were simple sodium silicate glasses with $\text{Na}_2\text{O}/\text{SiO}_2$ ratios in the range 1.0/1.0 to 1.0/2.1. These glasses were chosen because of their susceptibility to water attack and the ease with which they could be processed.

The raw materials used were of reagent grade. Their analyses are shown in Tables 1 and 2. These materials were hand mixed in a porcelain mortar pestle. The batches were fired in both alumina and high temperature porcelain crucibles. The firing temperature was 2050°F with a soak time of approximately thirty minutes. All firing was done in a small globar heated furnace.

After soaking for 30 minutes, the glass was formed into small disks. The mold used to form the disks was made of steel (See Figure 1). The glass was poured, pressed, allowed to cool slightly in the mold, and annealed at 800°F for thirty minutes. The furnace power was turned off, and the furnace was allowed to cool at approximately 158°F per hour. After cooling, the glass disks were removed and placed in a desiccator until such time as the tests were made.

The surface area of the sample exposed to the water in experiments had to be constant, or some geometric time factor had to be considered to account for changes in the surface area. It was decided to try to isolate one surface of a piece of glass and work with that surface only. In this way several things would be accomplished: the surface

SILICA

Silica	99.4000%
Chloride	0.0005%
Sulfate	0.0030%
Calcium	0.0100%
Heavy metals (as lead)	0.0010%
Iron	0.0050%
Magnesium	0.0005%
Potassium	0.0050%

SODIUM CARBONATE

Sodium Carbonate	99.5000%
Insoluble matter	0.0100%
Lost on heating at 285°C	0.5000%
Chlorine	0.0010%
Nitrogen compounds	0.0010%
Phosphate	0.0005%
Sulphate	0.0020%
Ammonium hydroxide precipitate	0.0100%
Arsenic precipitate	0.0001%
Calcium and magnesium precipitate	0.0100%
Heavy metals (as lead)	0.0005%
Iron	0.0005%
Potassium	0.0050%
Silica	0.0050%

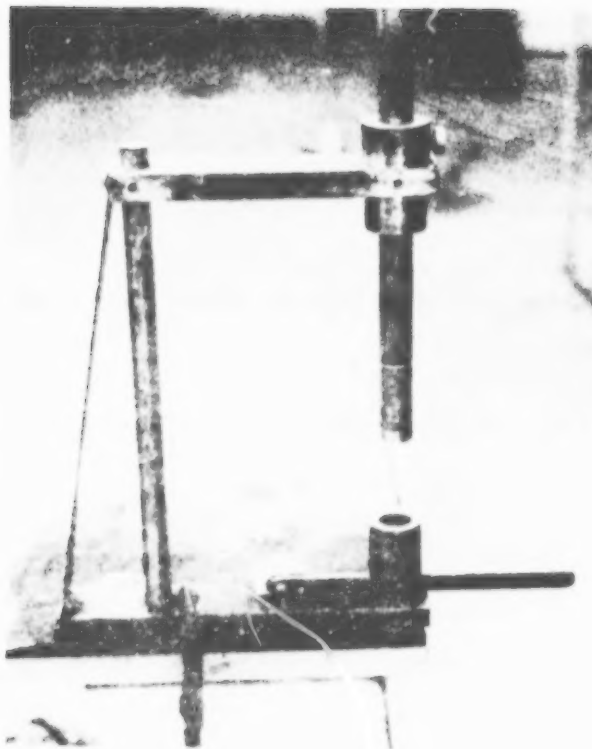


Figure 1. Photograph of the mold used to form the glass disks.

area exposed to the water at any time would be known, and the laboratory fabrication problem of producing samples with identical total volume (or total surface area) each time could be circumvented.

A disk shape was selected because it had the advantage of being a regular shape which was easily fabricated. All that was needed was a cylindrical glass mold in which a sample of any desired thickness could be formed. Having chosen to work with the disk shape, it soon became apparent that, if the sides and bottom of the disk were covered, it would leave only one surface of known area exposed to the aqueous solution. It, therefore, became standard procedure to cover the side and bottom of the disk with an insoluble epoxy resin (trade-name KOLDMOUNT) before each test in order to isolate one surface area (See Figure 2).

There were three experimental methods used to measure the rate of reaction of the glass with water. The first two involved the measurement of the sodium ion concentration in the aqueous solution. The third method employed the measurement of the total bulk weight lost by the sample during exposure to water.

To analyze the rate of reaction of the sodium silicate glass with water, the sodium ion concentration of the water both before and after exposure to the glass surface was measured. This sodium concentration was plotted versus time to give some idea of the rate of reaction of the glass when exposed to water.

In these experiments, the water to which the glasses were exposed contained only about 18 parts per billion sodium ion concentra-

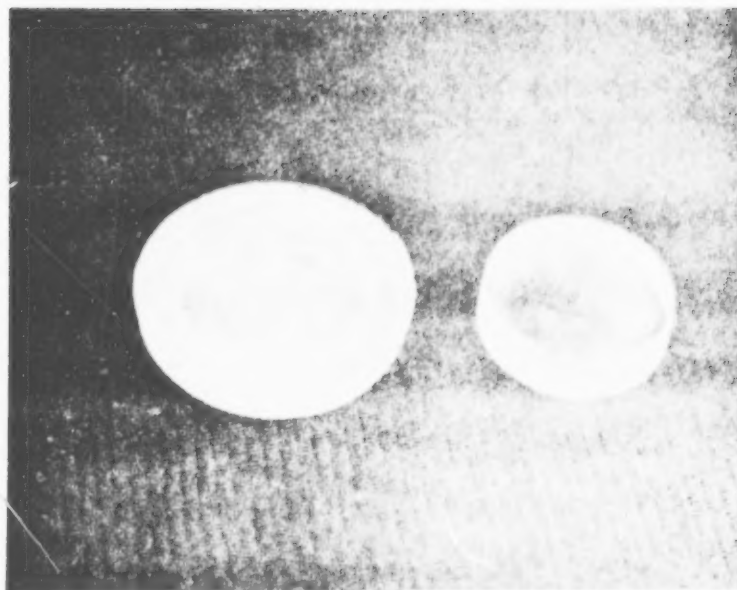


Figure 2. Photograph of the soluble glass before and after KOLDMOUNT has been applied.

tion. Therefore, eighteen ppb was used as the zero point or starting point for sodium concentration in all readings taken.

A coated glass disk was placed in a flask to which 200 milliliters of distilled water had been added. This flask was placed in a controlled temperature bath and left for a certain time interval (See Figure 3). When the appropriate time interval had elapsed, the sample solution was extracted in approximately the same manner each time. The solution was analyzed for the sodium ion content present by the Beckman Sodium Ion Analyzer. In this manner it was possible to study the rate of dissolution at different temperatures and at different times.

The Beckman Sodium Ion Analyzer has the capability to measure from 1 to 10,000 parts per billion sodium ion concentration. This analyzer is a process instrument that can make a continuous measurement of the concentration of sodium ions in a solution by determining the difference in potential developed between two electrodes, a silver/silver chloride electrode and a sodium ion electrode, immersed in the solution being analyzed (See Figure 4).

The operating principle of the analyzer is that the sodium ion measurement is made with a glass electrode-reference electrode pair. The glass electrode is of a special glass that is very responsive to changes in sodium ion concentration. This response comes in the form of a potential which is proportional to the log of the sodium ion concentration present in the sample. A reference electrode is also used to complete the circuit and provide a constant reference potential.

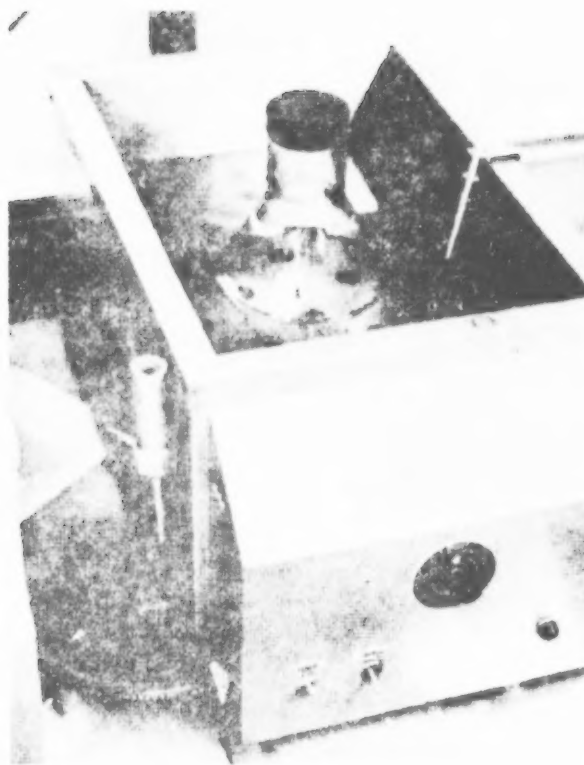


Figure 3. Photograph of the experimental apparatus used to measure water attack under static conditions.

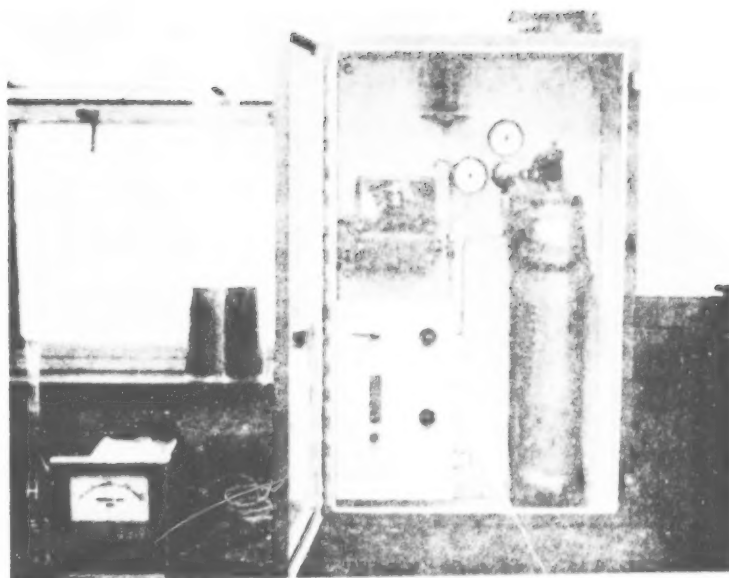


Figure 4. Photograph of the Beckman Sodium Ion Analyzer.

The sodium ion electrode is also sensitive to hydrogen ions (pH^+). In order to permit effective sodium ion measurement regardless of the pH^+ of the sample, it is necessary to control the pH^+ of the sample. In the Sodium Ion Analyzer, a simple system provides for adjustment of pH^+ by the addition of anhydrous ammonia. The electrode is not sensitive to the ammonia ion or other cations, with the exception of silver, which was not present in the sample.

The system operates in the following manner. The sample passes through the flow chamber which contains the sodium ion electrode and the reference electrode. Sample flow is controlled and the pH^+ of the system is raised by bleeding ammonia into the stream through a capillary tube. As the sample passes through the chamber, the sodium electrode senses changes in sodium ion concentration. The difference between the fixed potential of the reference electrode and the varying potential of the sodium electrode results in a signal which is sent to a high impedance amplifier. The amplifier gives a direct meter scale readout. It is a system similar to many standard pH^+ systems currently in use (23).

The concentration of sodium in solution after a given time was thus determined for a reasonably static situation. It then was necessary to determine what effect turbulent conditions would have on the rate of attack of the glass by water.

In this part of the study it was desirable to control the turbulent conditions as much as possible. A system was developed which could pump the water at a constant rate into the system at a given

point. The system in this instance was a water vat of approximately 10 gallons volume. It was found that an aquarium pump could be set up to work very adequately. A tube from the pump was attached so that water flowed into the system 1/8 inch above the glass sample, which had been coated as explained before and mounted on a stainless steel pedestal. Samples of the solution were withdrawn from the same position in the system each time. This withdrawal was from a point 1/4 inch above the sample. The water vat was heated by a resistance element. In addition, the temperature was controlled to $\pm 1^{\circ}\text{C}$.

By using this apparatus (See Figure 5), the rate of water attack upon the soluble glass at given times and temperatures could be observed under turbulent conditions. The sample was exposed to the water at a constant temperature, under constant turbulent conditions, for varying times. Sample solutions were extracted and then analyzed for sodium ion concentration by the Sodium Ion Analyzer, and plots were made of sodium ion concentration versus time.

The rate of water attack upon the bulk glass composition was tested. This procedure entailed suspending a glass sample in water under varying conditions. While being exposed to water attack, the weight of the sample suspended in the solution could be monitored and the overall weight loss of the bulk composition could be determined at variable times. There was data collected under the following conditions: (1) the sample was placed in a small amount of water (300 ml) at 24°C ; (2) the sample was placed in a large amount of water (14 liters) at 24°C ; (3) the sample was placed in a small amount of

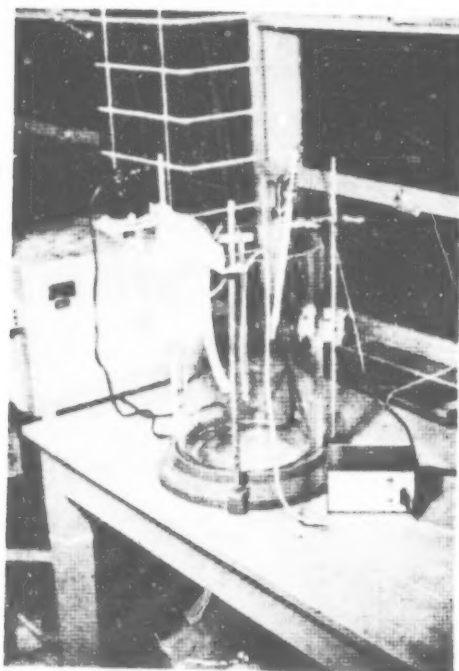


Figure 5. Photograph of the experimental apparatus used to measure water attack under turbulent conditions.

water (300 ml) at a high temperature (72°C); (4) the sample was placed in turbulent water (14 liters) at 24°C ; and (5) a different glass composition was placed in 300 ml of water at 24°C and compared with the more soluble composition.

The samples were in each case weighed continuously by an Ainsworth analytical balance that was connected to a strip chart recorder which plotted the weight loss versus time. This work was done so that the results of the decomposition of the total bulk could be compared to the loss of sodium ions from the sample.

Spectrographic analyses were run on solutions which had been exposed to different glass compositions. The glass samples were exposed to water for various times, and sample solutions were withdrawn. A drop of this solution was then analyzed by use of a Bausch and Lomb dual grating spectrograph. The resulting photographic plates were analyzed for the relative intensities and were qualitatively related to the amount of the element present in the solution. These comparisons coupled with the other data enabled an understanding of how the attack of water upon soluble glass proceeds.

PRESENTATION AND DISCUSSION OF RESULTS

The samples used in this experimental research were sodium silicate glasses of varying composition. In the discussion text these samples will be referred to as being of a rapid dissolving, a moderately soluble, or a more durable composition. The rapid dissolving glasses are those having a $\text{Na}_2\text{O}/\text{SiO}_2$ molar ratio of between 1.0/1.0 and 1.0/1.3. The moderately soluble glasses are those which have a ratio of 1.0/1.3 to 1.0/1.6, and the more durable compositions have molar ratios greater than 1.0/1.6. Any of these glass compositions will become more durable, less soluble, if there are impurities present in the glass.

The first experimental measurements were made on a moderately soluble glass disk exposed to distilled water at a temperature of 72°C . The only current flow or turbulence in the system was that set up by a thermal gradient in the system. This gradient was minimized by the immersion of the flask in the water bath to give more isothermal conditions.

In these measurements, the disks were oriented horizontally on the bottom of the flask. Although strictly speaking it cannot be said that the surface remained exactly constant, the change in surface area was so slight as to not warrant consideration. This statement can be made because it was observed that the glass dissolved rather evenly across the exposed face. This characteristic helps to minimize

any additional concentration caused by an increase in surface area due to a curved surface being exposed rather than a planar surface. It was noted that after a certain period of exposure to the water a surface film or coating was being deposited on the glass disk. This surface deposit remained for the entire duration of the experiment. If the glass was allowed to completely dissolve, the film would remain in the bottom of the epoxy shell. After dehydration, the residue became a brittle, white, flaky substance. Other workers have indicated in the literature that the substance is probably a complex sodium carbonate-fine grain silica residue.

Samples of the solution in the flask were withdrawn at various times and analyzed for sodium ion concentration. These concentrations were then plotted versus time to yield the curve seen in Figure 6. The ordinate in this figure is sodium ion concentration in parts per million as measured by the Beckman Sodium Ion Analyzer. The abscissa is time of exposure to water in hours. The time at which the sample is placed into the water in the flask is considered the zero point. Initial sodium ion concentration is taken as 18 ppb, the initial concentration of sodium in the distilled water. If the concentration of sodium is considered C , and the time is considered T , then the slope of the curve dC/dT will yield the rate at which sodium ions are coming into solution from the glass. This may be the rate of solubility of the glass, or it may be the rate of water attack on the glass surface. Its exact correlation with the solubility of the glass is not known. All that can be said is that the rate observed is the rate at which

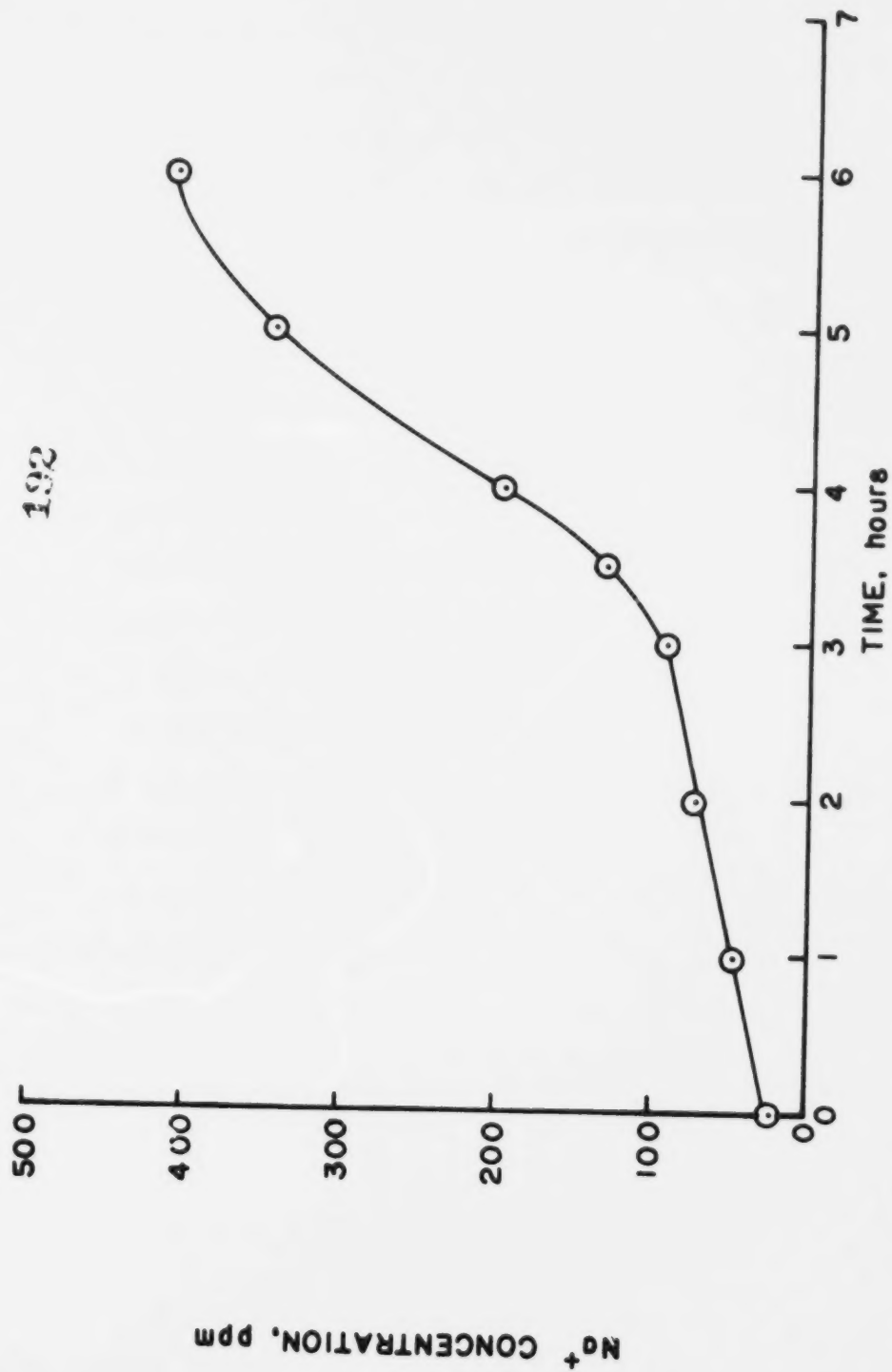


FIGURE 6. PLOT OF SODIUM ION CONCENTRATION VERSUS TIME AT 72°C UNDER STATIC CONDITIONS.

sodium ions are going into solution under these specific conditions. It is quite possible that slight changes in the experimental conditions will yield changes in this rate.

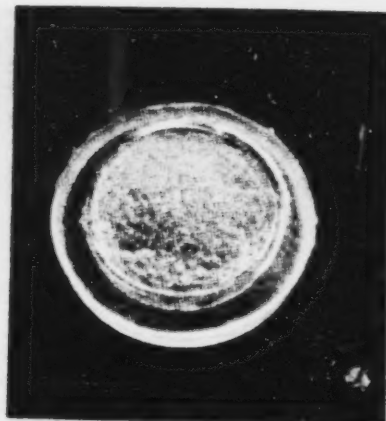
In Figure 6, it can be seen that from the time the sample was placed into the water until after about 2 hours of exposure, the rate of increase of the sodium ion concentration was constant. The initial increase was caused by the removal of sodium ions from the glass by the aqueous solution. The removal of these sodium ions from the surface causes the glass to develop a glass-solution interface which is depleted of alkali ions and is rich in silica. The macroscopic effect of this leaching is the formation of a boundary layer through which sodium ions and water molecules must diffuse for the dissolution to proceed (See Figure 7). As the boundary layer is formed, the rate slows to an almost negligible increase in sodium ion concentration because diffusion is occurring.

After three hours exposure time, the rate begins to increase again. This rapid increase in rate can be attributed to two factors. One factor is that as more sodium enters the solution the more basic the solution becomes. This basic solution is much more corrosive to the actual silica framework than water alone. As the framework is corroded at a faster rate, more sodium is released into solution at a faster rate.

The increase in rate at this point is also caused by the breakdown of the boundary layer (See Figure 8). After the boundary layer has been exposed to the water for a time, it begins to deteriorate



(A)



(B)

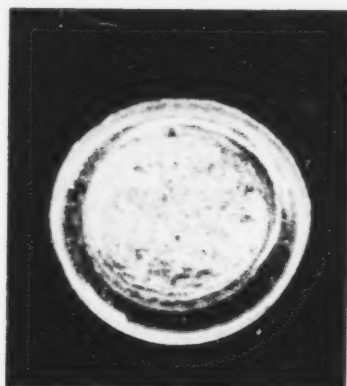


(C)

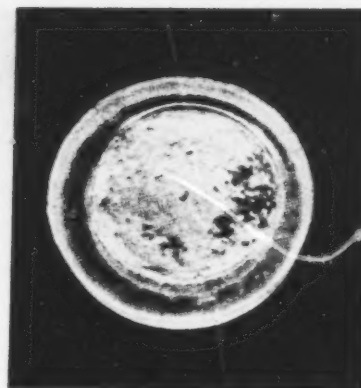


(D)

Figure 7. Photographs of the boundary layer forming on the surface of a more durable glass (A) originally, (B) after 1 hour, (C) after 2 hours, (D) after 4 hours.



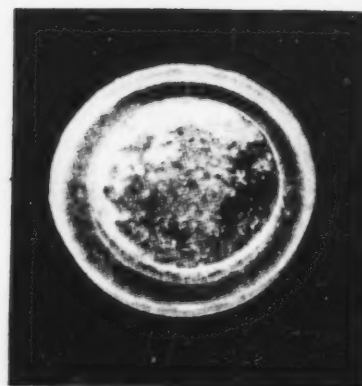
(E)



(F)



(G)



(H)

Figure 8. Photographs showing breakdown of the boundary layer on a more durable glass (E) after 5 hours, (F) after 6 hours, (G) after 7 hours, (H) after 8 hours.

and allow water to diffuse through it at a faster rate. This deterioration then allows the glass matrix to be attacked at a faster rate and yields the higher sodium concentration in solution.

This theory can be supported by spectrographic analysis for the silica content of a solution. For times coinciding with the initial leaching of sodium from the glass and for times coinciding with the formation of a boundary layer, it was observed that there is very little increase in the amount of silica in solution. However, for times coinciding with the breakup of the boundary layer and alkaline attack of the silica framework, there is a very substantial increase in the amount of silica in solution. This indicates that there is an extended period of exposure during which very little silica goes into solution followed by a period during which silica is rapidly dissolved.

After about 5 hours, the rate gradually slows as there is degradation of the surface of the sample. At this time the sample has been corroded to the extent that it no longer presents a continuous surface to the solution. Water is able to go completely through the sample and attack the sample on more surfaces. Also the sample has been almost completely eroded away. Therefore, at this point the test ceases to be valid.

Figure 9 shows the effect obtained by increasing the temperature. The immediately noticeable effect is that the reaction takes place much faster at higher temperatures. For example, after one hour of exposure at 72°C there was approximately 50 ppm sodium concentration in solution. After one hour at 90°C there was an average 115 ppm

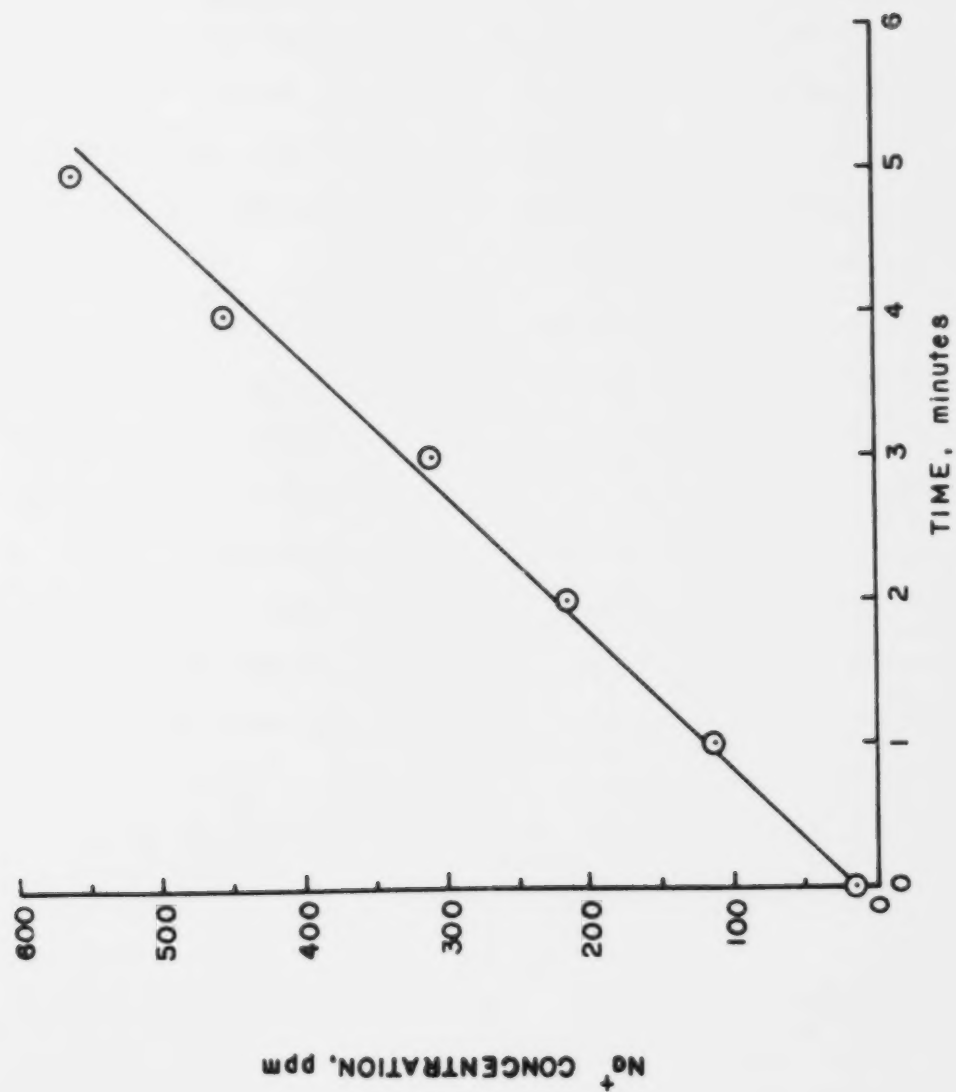


FIGURE 9. PLOT OF SODIUM ION CONCENTRATION VERSUS TIME AT 90°C UNDER STATIC CONDITIONS.

sodium concentration in solution. This represents a very marked effect by temperature increase of just 18°C . This increase in rate is reflected in the greater slope (dC/dT) of the curve. There is no change in the rate of sodium uptake over the duration of the experiment. The sodium concentration increases at a linear rate. This indicates that at higher temperatures there is not an induction period involved during which diffusion through a boundary layer slows the reaction. This effect could be due to several reasons. It could be that the boundary layer in fact never forms at this temperature. The author considers this very unlikely from the standpoint of the surfaces which have been studied and photographed (See Figure 7). It is possible that at this temperature a boundary layer does form, but it is broken down by water turbulence so that it has no effect on the reaction rate. Finally, at this temperature viscosity of the water may have been reduced sufficiently for it to diffuse through any boundary layer that is present at such a fast rate that the boundary layer diffusion is no longer a rate controlling step. The pronounced effect of temperature is demonstrated by the results shown in Figures 6 and 9. With the exception of temperature, these two experiments were performed under the same static conditions.

The effect of turbulence on the rate of reaction of the glass with water was observed next (See Figures 10, 11, and 12). The most evident result of the turbulence is a dramatic increase in the rate of sodium uptake. From Figure 6, it can be seen that it takes one hour under static conditions for 50 ppm sodium ion concentration to show

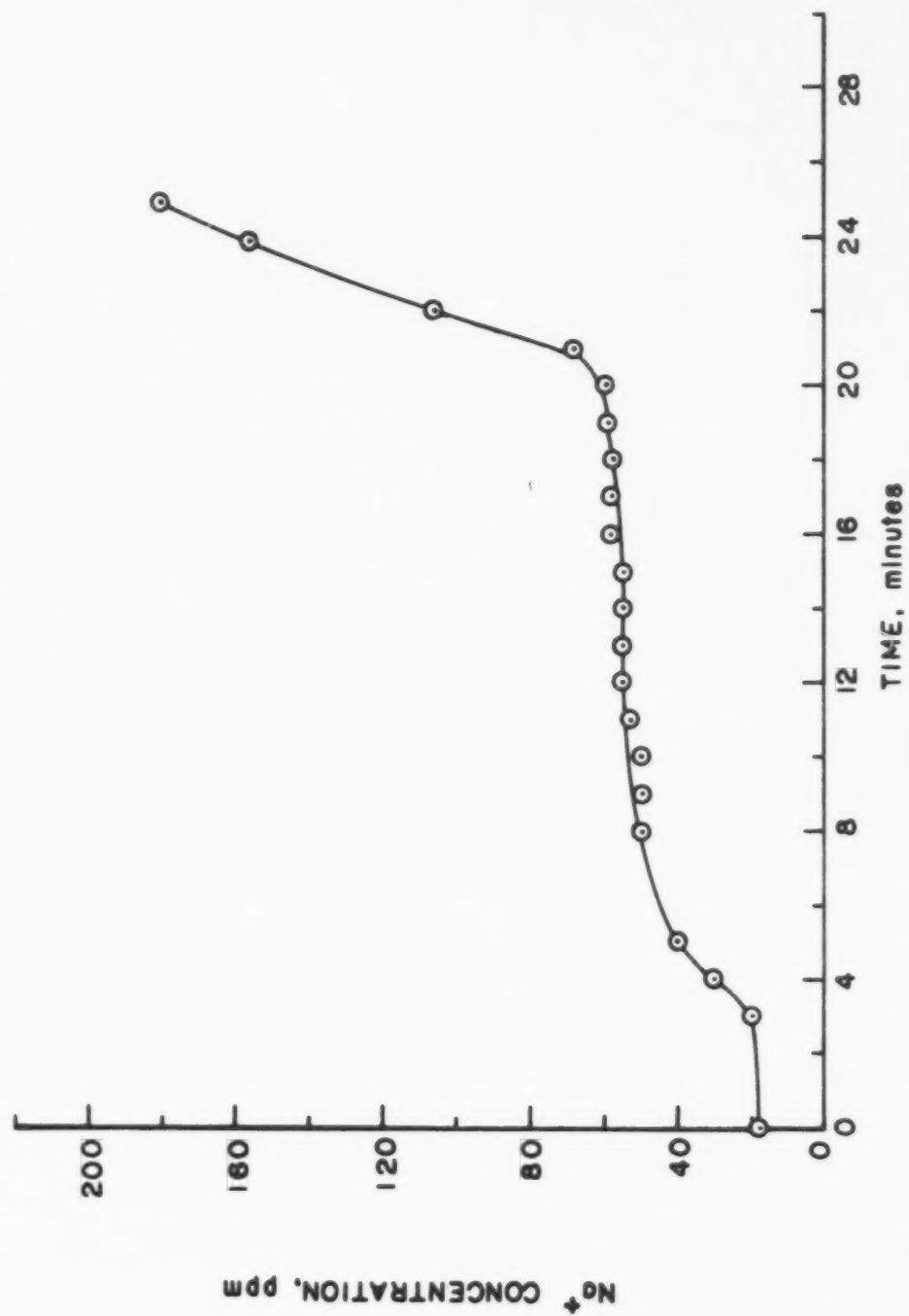


FIGURE 10. PLOT OF SODIUM ION CONCENTRATION VERSUS TIME AT 65°C UNDER TURBULENT CONDITIONS.

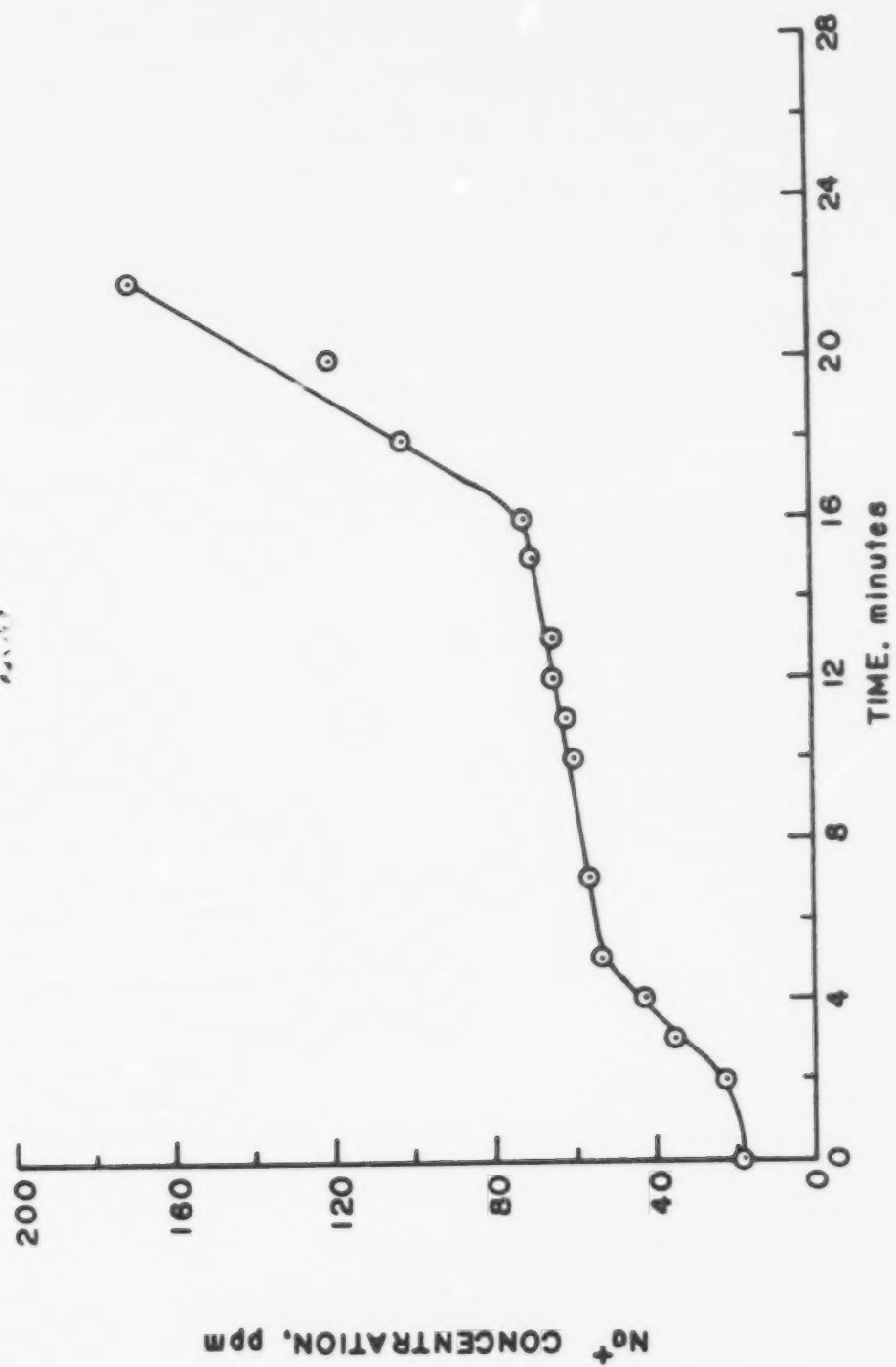


FIGURE 11. PLOT OF SODIUM ION CONCENTRATION VERSUS TIME AT 70°C UNDER TURBULENT CONDITIONS.

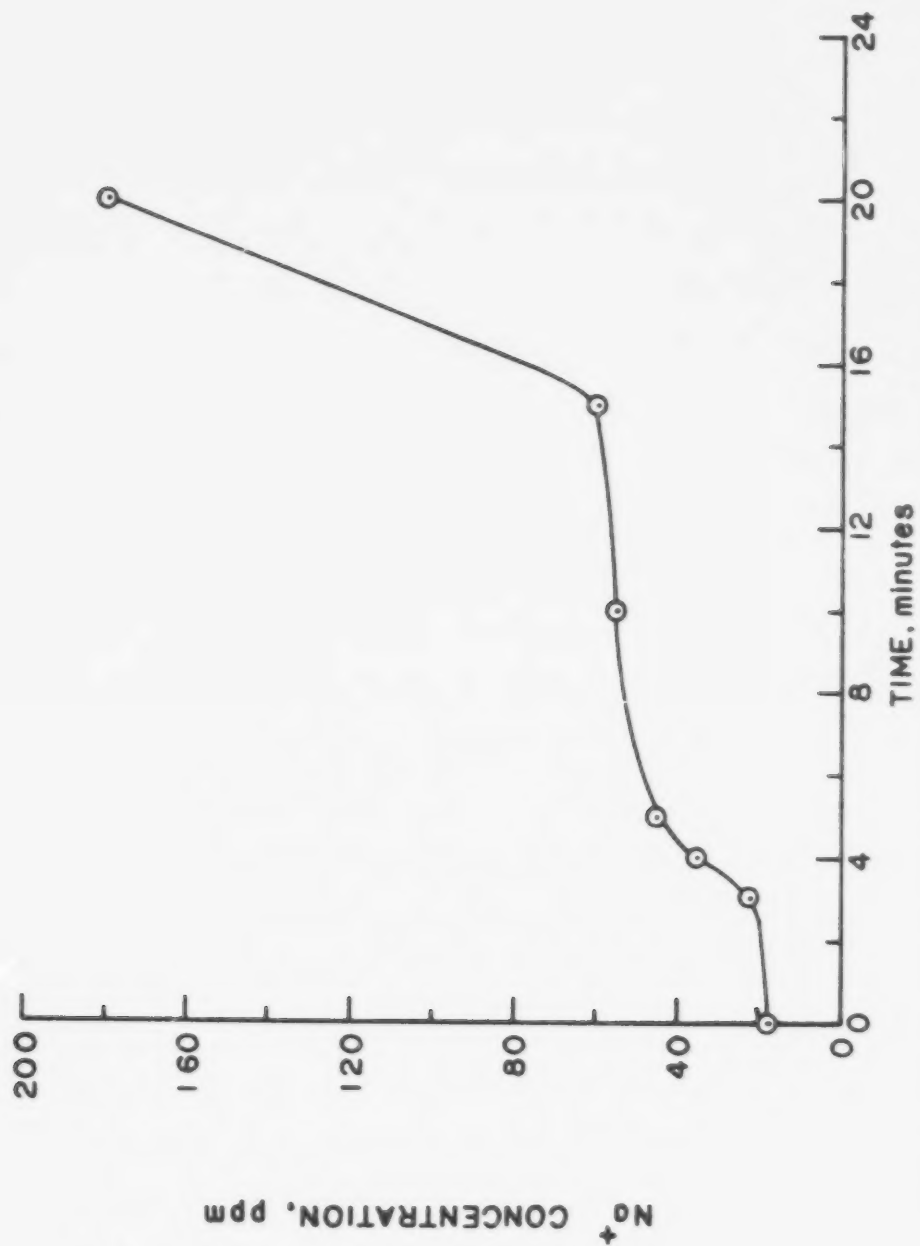


FIGURE 12. PLOT OF SODIUM ION CONCENTRATION VERSUS TIME AT 75°C UNDER TURBULENT CONDITIONS.

up in solution. In Figure 10, it is found that under turbulent conditions there is 50 ppm sodium ion concentration in solution after only eight minutes. This is an increase of 7.5 times as fast under turbulent conditions. At this point, once again the buildup of a boundary layer is sufficient to have a leveling effect on the curve. The rate of increase of sodium ion concentration becomes quite small until twenty minutes of exposure time has passed. At this time, there is once again a very rapid increase in the slope of the curve. This increase is probably due to the breakdown of the barrier layer. This deterioration occurs rapidly because of the turbulent conditions around the surface. The constant flow of water against the surface causes enough abrasion to deteriorate the boundary layer and expose the glass to attack as exhibited by the very steep slope after 20 minutes exposure in Figure 10.

Figures 10 and 11 show again in a clear manner the influence on the attack process of even very minor temperature changes. If the point at which the slope begins to increase again after the induction period is used as a reference, it can be seen that an increase in temperature serves to shift the reaction to a shorter time along the abscissa. For example, in Figure 10 (run at 65°C) that change in slope occurs at 20 minutes exposure time. In Figure 11 (run at 70°C) that slope change occurs after only 16 minutes exposure time. In Figure 12, the time has been reduced to only 14 minutes of exposure to water attack. So it can be seen that the effect of turbulence and temperature in the system is very pronounced. These results indicate that tur-

bulent conditions promote the dissolution of the glass. All of the results discussed thus far were obtained by analyzing the solution in contact with moderately soluble glass after certain exposure times. This analysis was made with the Beckman Sodium Ion Analyzer.

The remainder of the results were concerned with changes in the total bulk composition of the glass. In particular, the weight loss of the glass was monitored by an Ainsworth analytical balance which weighed the sample continuously. This weight loss was plotted versus time of exposure to water. Typical results of this analytical technique can be seen in Figure 13.

In Figure 13, a sample of rapidly dissolving glass was placed in 300 ml of distilled water at 24°C. The sample was weighed continuously. The resulting curve is linear until 120 minutes of exposure has occurred. At this time, the sample had decomposed to the extent that there was no longer a continuous surface presented to the corroding medium. By this it is meant that the surface crumbled and depleted to the extent that the test could not be considered valid for longer times.

The effect of turbulence was attempted to be shown, but the experimental apparatus could not be operated continuously due to the swaying effect caused by the water flow. Two weight measurements were made after 20 and 50 minutes of exposure under turbulent conditions. These measurements are superimposed on Figure 13. There is not enough data to make any conclusions except that, as in the previous experiments, turbulence seems to have increased the rate of

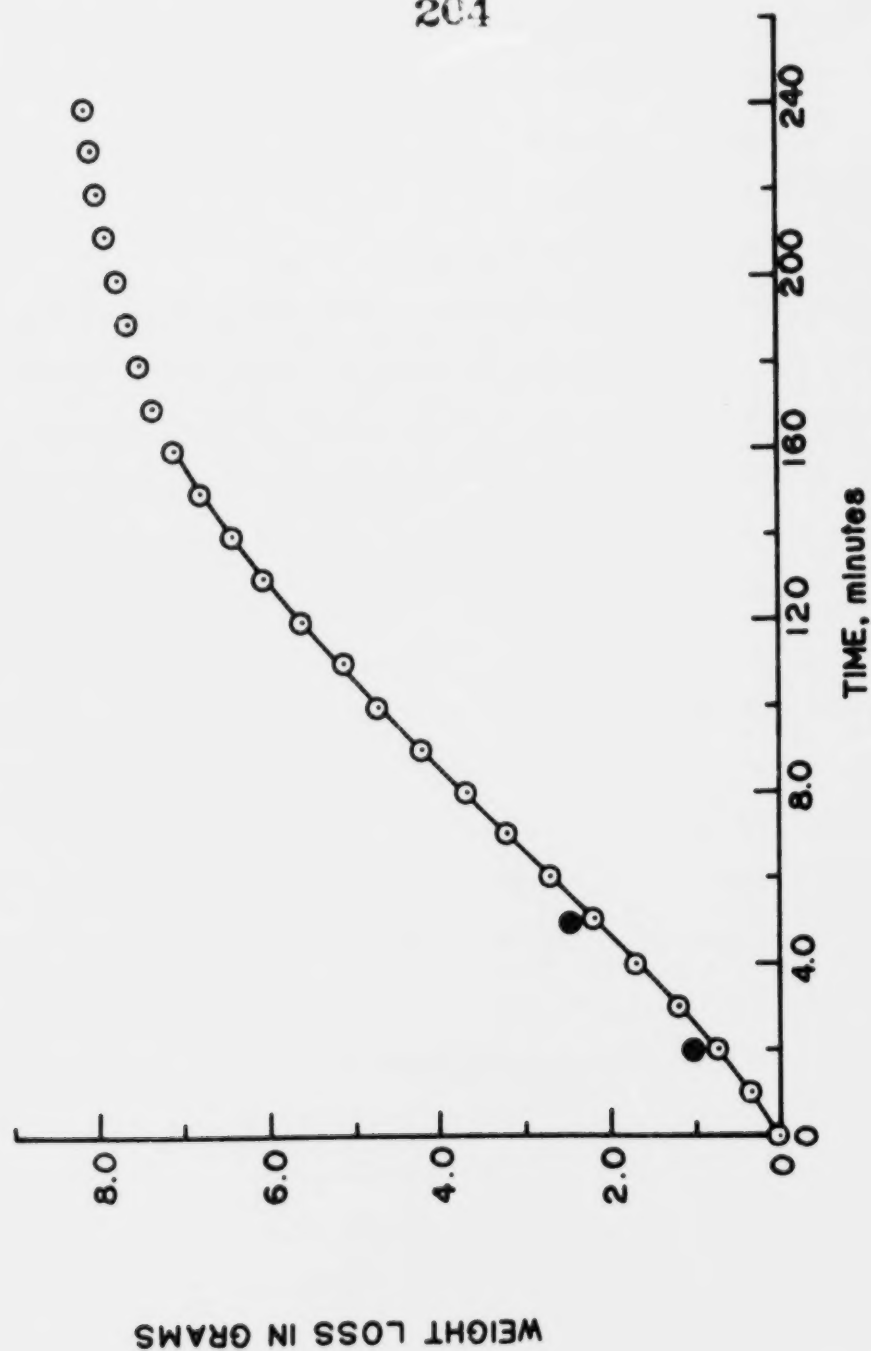


FIGURE 13. PLOT OF BULK WEIGHT LOSS VERSUS TIME AT 24°C IN 300 MILLILITERS OF WATER.

attack on the glass.

Next, the effect of an increase in temperature was observed using the weight loss measurement method. The water was preheated to 72°C and then brought into contact with the glass sample. The effect was as expected. The glass lost weight at a much faster rate at 72°C than at 24°C (See Figure 14). An example of this is that at 24°C the glass sample had lost 1.7 grams after 50 minutes of exposure. However, if exposed to 72°C water for only 5 minutes, the same glass lost 1.8 grams. The rate of bulk weight loss at this temperature once again displays linear characteristics.

The effect of the volume of solvent (or corroding medium) to which the sample is exposed was also investigated. It was of interest to observe if the amount of water to which the glass was exposed had a great effect on the rate of attack. Of particular interest was whether or not the process was self-limiting in small volumes of water. If so, it would indicate that the water was becoming saturated with the solute and causing the reaction to change, probably to slow or stop completely.

It was found that, if the sample were placed in 14 liters of water instead of in 300 ml of water, there was very little change in the rate of weight loss observed. If the curves in Figures 15 and 13 are compared, it is found that they could almost be superimposed over each other without any change. The only effect that was observed was that with the larger volume of water (14 liters) the loss took place at only a minutely faster rate; the increase was to be expected. The

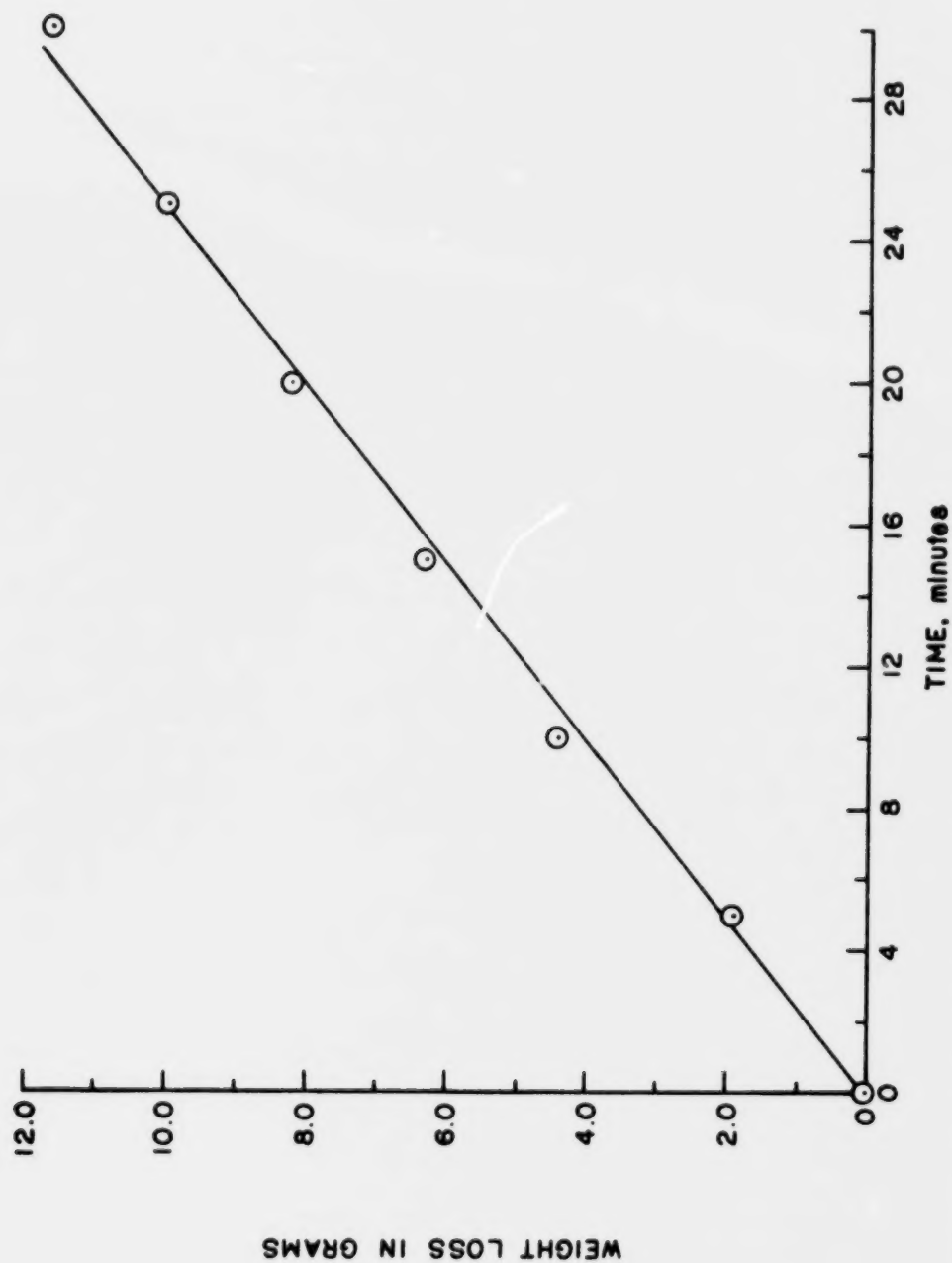


FIGURE 14. PLOT OF BULK WEIGHT LOSS VERSUS TIME AT 72°C IN 300 MILLILITERS OF WATER.

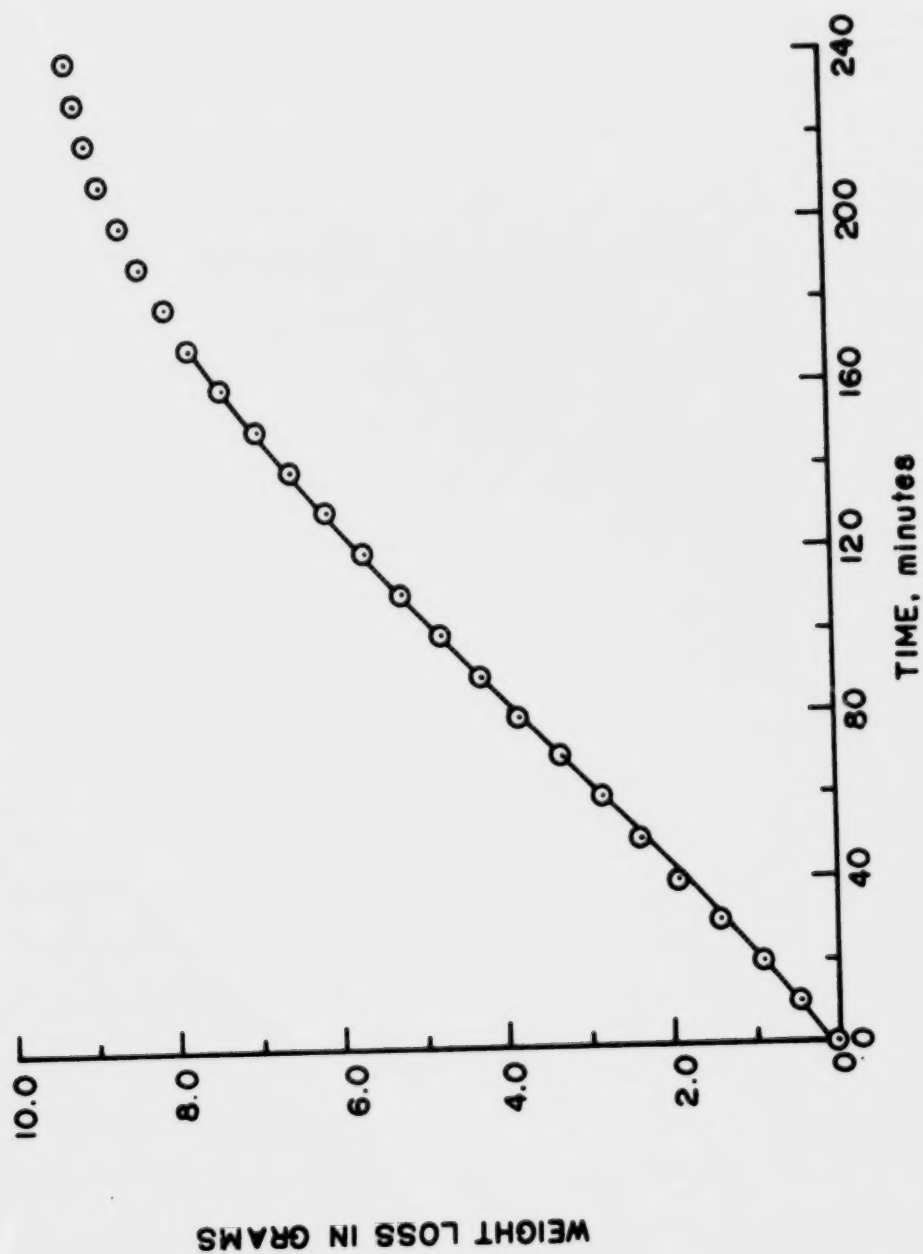


FIGURE 15. PLOT OF BULK WEIGHT LOSS VERSUS TIME AT 24°C IN 14 LITERS OF WATER.

slightness of this increase is surprising. The lack of effect of solute volume is shown in the following example: After 40 minutes, 1.7 grams weight loss is observed in 300 ml of 24°C water. If the sample is exposed to 14 liters of 24°C water, the weight loss increases only 0.2 gram to 1.9 grams weight loss. After 140 minutes in 300 ml of water, the weight loss is 6.4 grams; in 14 liters, it is 6.5 grams.

This very small difference in weight loss between the two volumes leads to the conclusion that the amount of solvent present has very little effect on the rate of attack on the glass sample. At least this appears to be true for the amounts of water used in these experiments. It is possible that at even smaller volumes of water there is a self-limiting effect. However, these experiments indicate that, as long as there is enough solvent present to dissolve the glass, it does not matter how much excess solvent is present in the system.

The weight loss measurement was also plotted versus time for a less soluble glass. This glass was 68 per cent silica and 32 per cent soda. The results of this measurement showed an initial loss, followed by an extended period of very little or no weight loss and a final rapid weight loss (See Figure 16). The various sections of the curve can be explained by applying the boundary layer diffusion theory outlined previously. In fact, this curve is remarkably similar to those obtained by sodium ion analysis. It appears to follow the same sequence as the rate of sodium ion increase shown in Figure 6.

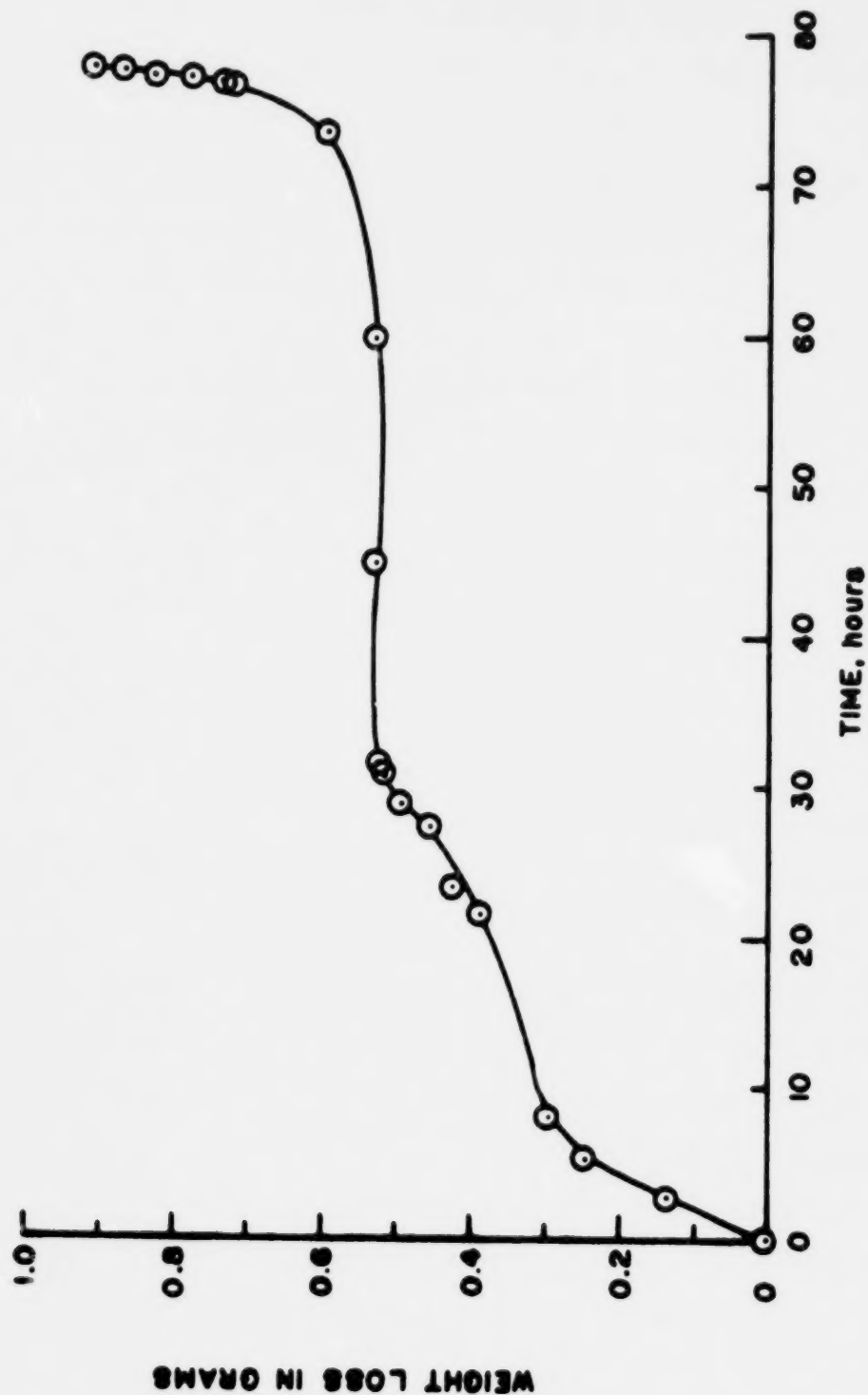


FIGURE 16. PLOT OF BULK WEIGHT LOSS VERSUS TIME AT 72°C IN 300 MILLILITERS OF WATER FOR A MORE DURABLE 66% SILICA GLASS.

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There is an initial weight loss, a leveling-off effect (a boundary layer induction period), and a final sharp increase in the rate of weight loss.

If the results of the weight loss measurements of rapidly dissolving glass (Figure 14) and more durable glass (Figure 16) are compared, it is observed that there is a difference in the way that the two types of glass dissolve. The rapid dissolving glasses lose weight at a constant linear rate. More durable glasses go through a change in surface characteristics which causes it to dissolve in steps.

The constant linear rate of weight loss in rapidly dissolving glasses is indicative of a true solution process (See Appendix I). By simple solution it is being implied that there is no breakdown of the glass structure into its individual components as far as the solvent is concerned. Both soda and silica complexes are being attacked as one single phase much as a single sugar crystal is dissolved in water (See Figure 17 and Appendix II). This theory is verified by spectrographic analysis which shows that in rapidly dissolving glasses the silica concentration in solution increases at a relatively constant rate. In more durable glasses the silica concentration remains low until such time as the silica framework is attacked by solution. This attack is exhibited by a dramatic increase in silica concentration in solution.

The conclusion reached from this comparison is that sodium silicate glasses which dissolve rapidly without the formation of a boundary layer dissolve by a mechanism quite similar to true solution.

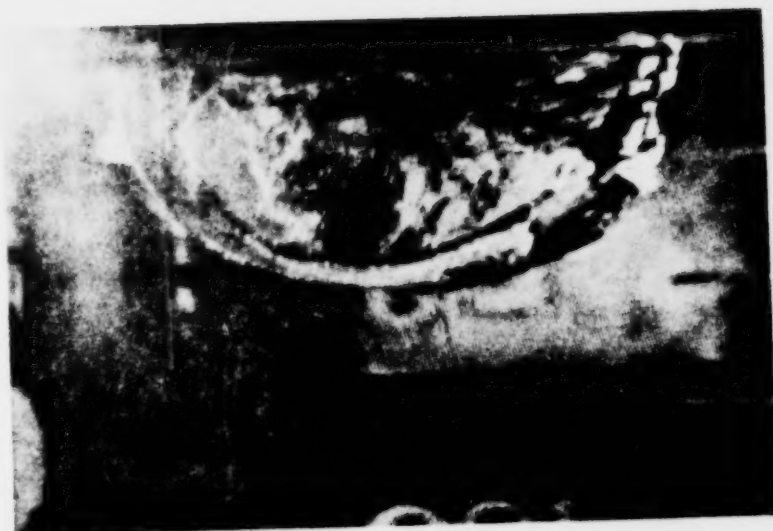
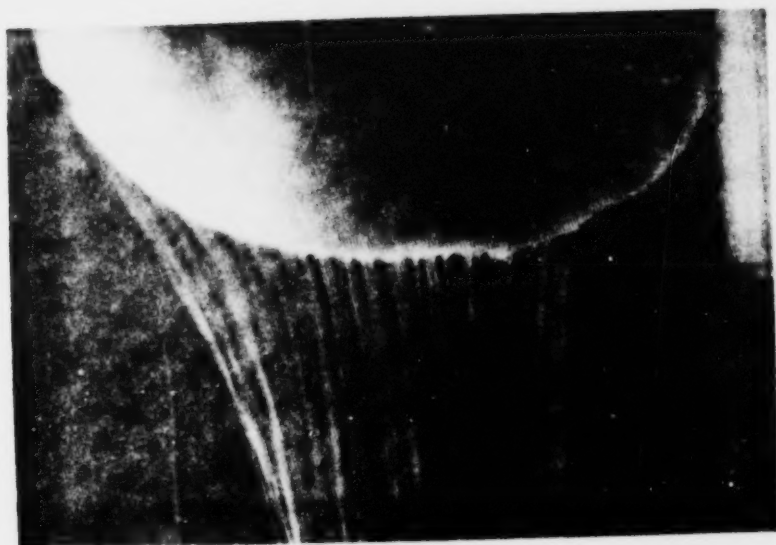


Figure 17. Photograph showing the similarity of concentration gradients flowing from the surface of sugar (A) and rapidly soluble glass (B).

In more durable glasses there is the formation of a boundary layer which causes the dissolution of the glass to be more complex. This process can be described as the preferential leaching of sodium ions, followed by the formation of a boundary layer, and ultimately alkaline attack on the remaining silica network.

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CONCLUSIONS

1. The attack of water on a rapidly soluble silicate glass released sodium ions into the solution at a linear rate. Weight loss also followed a linear relationship versus time. This linearity represents a simple solution process and not a complex decomposition process as observed by experimentors working with more complex glasses.
2. In more durable but yet soluble glasses, there is the formation of a boundary layer after a certain time of exposure to water. It then becomes necessary for the water molecules to diffuse through the boundary layer before the solution process can continue.
3. The effect of temperature is that the rate of reaction of the glass with the water is greatly increased as the temperature is increased. This result is to be expected if the dissolution of the glass is an endothermic reaction. It was also found that temperature can affect the boundary layer and water viscosity to the extent that water can diffuse through to the glass surface at a fast enough rate to maintain a constant rate of reaction with the glass.
4. The effect of turbulence was demonstrated to be a substantial increase in the rate of attack of the water on the glass surface under turbulent conditions. The explanation of this is that turbulence produces more abrasion on the surface. Subsequently,

the water molecules are able to cluster around the sodium silicate molecules more easily and carry them into the solution.

5. Volume dependency was shown to not be as great as was originally thought. The solution process did not seem to be self-limiting in small volumes of water. In fact, the amount of solvent present appears to have very little effect at all on the rate of attack on the glass. Larger volumes of water did show a slight increase in the amount of glass dissolved, but the increase is not very significant.

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RECOMMENDATIONS FOR FUTURE WORK

The principles observed in this investigation should ultimately aid in the utilization of soluble sodium silicate glass in the glass industry as a partial answer to the solid waste dilemma.

The significance of this work is that it demonstrated the feasibility of producing a rapidly dissolving glass which could be easily decomposed without undue pollution of water resources.

Having established this fundamental ability to produce such a glass, correlated study can be accomplished to develop more suitable glasses and study the solution characteristics of those glasses. Corresponding studies are being conducted in the area of coating materials and procedures for various soluble glass compositions.

The major deficiencies of the rapid dissolving glass appeared in two areas, fabrication and the ability to be coated. The solubility of the glass is such that it will easily meet any requirements as to speed of dissolution. In fabrication, however, the glass proved to be quite unstable requiring close attention to prevent devitrification. The forming of nucleation sites and subsequent devitrification was almost immediately evident if fabrication procedures were not closely controlled. Problems in the area of coatings developed because of the extreme hygroscopicity of the glass surface.

The solution of these problems will likely involve the development of more overall suitable glass compositions, equipment modifications, better coating procedures and materials, and probably a com-

bination of all of these.

Better quality control over the firing conditions and forming conditions of the glass is a definite requirement at this stage. A furnace is required which will not allow contamination of the batch and has better control over the heating and soaking periods. With more sophisticated forming equipment, sample quality control could be upgraded to eliminate sample variations in uniformity, annealing stresses, and surface condition. The elimination of these problems would greatly enhance the potential for success of the project.

The author is of the opinion that, for the optimum development of the project, new glass compositions which would dissolve more slowly should be investigated. A small pilot plant setup would be extremely helpful. This would be the next logical step if progress is to take place in the fabrication of a soluble glass container.

1. Abrahams, J. H. "Packaging Industry Looks at Waste Utilization." Glass Container Manufacturers Institute, Inc., Washington, D. C.
2. Vaughan, R. D. "Packaging and Solid Waste Management." U. S. Department of Health, Education, and Welfare, Consumer Protection and Environmental Health Service.
3. Silvermann, A. "Chemical Durability of Glass: An Outline." Bull. Am. Ceram. Soc. 30:399. 1951.
4. Bichowsky, F. R. v. "Note on the Mechanics of the 'Weathering' of Glass." J. Am. Ceram. Soc. 3:309. 1920.
5. Vail, J. G. Soluble Silicates: Their Properties and Uses, Volume I. Reinhold Publishing Corp., New York. 1952.
6. Morey, G. W. The Properties of Glass. Reinhold Publishing Corp., New York. 1954.
7. Scholes, S. R. Modern Glass Practice. Industrial Publications, Chicago. 1952.
8. Haller, W. "Kinetics of the Transport of Water Through Silicate Glasses at Ambient Temperatures." Physics and Chemistry of Glasses. 1(2):46-51. 1960.
9. Budd, S. M. "The Mechanisms of Chemical Reaction Between Silica Glass and Attacking Agents." Physics and Chemistry of Glasses. 2(4):111-114. 1961.
10. Rawson, H. Inorganic Glass-Forming Systems. Academic Press, New York. 1967.
11. Dietzel, A. and H. Wickert. Glastech. Ber. 29:1-4. 1956.
12. Bowen, N. L. "Devitrification of Glass." J. Amer. Ceram. Soc. 2:262. 1919.
13. Cox, S. F. "Devitrification of Glass." J. Amer. Ceram. Soc. 2:576. 1919.
14. Ford, K. L. "The Weathering of Glass Containers." J. Amer. Ceram. Soc. 5:837. 1922.
15. Baillie, W. L. "The Effect of Additives on Chemical Durability of Glasses." J. Soc. Glass Tech. 6:68-101. 1922.

16. Sen, S. and F. V. Tooley. "Effect of $\text{Na}_2\text{O}/\text{K}_2\text{O}$ Ratio on Chemical Durability of Alkali-Lime-Silica Glasses." J. Amer. Ceram. Soc. 38:175. 1955.
17. Lyle, A. K., W. Horak, and D. E. Sharp. "The Effect of Alumina Upon the Chemical Durability of Sand-Soda-Lime Glasses." J. Amer. Ceram. Soc. 19:142. 1936.
18. Niggli, P. "The Reaction of Sodium Carbonate and Silica." J. Amer. Ceram. Soc. 35:1693. 1913.
19. Howarth, J. T., W. Maskill, and W. E. S. Turner. "The Rate of Reaction Between Silica and Sodium Carbonate at Different Temperatures and the Process of Vitrification." J. Soc. Glass Tech. 17:25. 1933.
20. Douglas, R. W. and T. M. M. El-Shamy. "Reactions of Glasses with Aqueous Solutions." J. Amer. Ceram. Soc. 50:1-7. 1967.
21. Douglas, R. W. and J. O. Isard. "Action of Water and of Sulfur Dioxide on Glass Surfaces." J. Soc. Glass Tech. 33(154): 289-335. 1949.
22. Rana, M. A. and R. W. Douglas. "The Reaction Between Glass and Water." Physics and Chemistry of Glasses. 2(6): 179-205. 1961.
23. Beckman Instruction Manual: Trace Sodium Ion Analyzer. Beckman Instruments, Inc. Fullerton, California.
24. Maron, S. H. and C. F. Prutton. Principles of Physical Chemistry. The MacMillan Company. New York. 1958.
25. Sienko, M. J. and R. A. Plane. Chemistry. McGraw-Hill Book Co., Inc. New York. 1957.

SOLUTIONS

When several nonreacting substances are mixed, three possible types of mixtures may be obtained: (a) a coarse mixture, (b) a colloidal dispersion, or (c) true solution. In a coarse mixture, the individual particles are readily discernible and may be separated from each other by mechanical means. In a colloidal dispersion, the particles are much finer and the heterogeneity is not as apparent. It is, however, not a homogeneous dispersion. The true solution possesses the characteristic that the constituents cannot be separated by mechanical means. A true solution is a physically homogeneous mixture of two or more substances.

The extent to which a substance will dissolve in another varies greatly with different substances and depends on the nature of the solute and solvent, the temperature, and the pressure. The effect of pressure is usually small unless gases are being used. However, temperature usually has a marked effect. The direction in which the solubility of a substance in a solvent changes with temperature depends on the heat of solution. If the substance dissolves exothermally, the solubility at higher temperatures will decrease. If, however, the dissolution is an endothermic reaction, the solubility will increase as the temperature is raised.

A general rule is that likes dissolve likes. Which means that compounds similar in chemical character are more readily soluble in

each other than those of entirely different chemical character.

The extent to which solids dissolve in liquids varies greatly with the nature of the solid and liquid, the temperature, and to some extent the pressure on the system.

The influence of temperature on the solubility of a solute in some solvent is usually quite pronounced. Because most solutes tend to absorb heat on solution, they are more soluble at higher temperatures. The opposite is true of exothermic reactions, but all behavior is not regular in this respect.

Whenever the solubility of any substance is plotted versus temperature, the curve is continuous until there is a change in the nature of the solid phase. As soon as the solid changes, a break will appear in the solubility curve and a new solubility curve will originate from this point. These breaks are characteristic of the substance involved.

The particular change in the nature of the solid phase involved could be a number of things. It could be a transformation from one crystalline form to another; it could be a change from a hydrate to an anhydrous salt; or it could be a change from one hydrate to another (24).

THE SOLUTION PROCESS

When sugar is placed in a beaker of water, the sugar dissolves. In this process of solution, the sugar lattice is ripped apart, and the individual sugar molecules are distributed throughout the body of the solution. The entire process can be theorized to occur in the following way: First, a sugar molecule must be pulled from the surrounding molecules. Since there is molecular attraction between molecules in the crystal lattice, work must be done to overcome this intermolecular attraction (solute-solute attraction). Second, water molecules have to be displaced to accommodate the sugar molecule. This displacement also requires the expenditure of energy, since there is molecular attraction between water molecules (solvent-solvent attraction). If both of these processes require energy, they cannot be the driving force for the solution to occur. There has to be a third step which provides the energy that is needed. This step is called solvation. Solvation arises from the attraction between the sugar molecules and the water molecules. This sugar-water attraction provides almost enough energy to overcome the sugar-sugar attraction and the water-water attraction. The last bit of energy necessary is supplied by a reduction in the average kinetic energy of all the molecules in the system.

The actual state of the particles once they get into the solution is one of the really challenging problems facing chemists

today. Progress is very slow. Present theory assumes that solution occurs by some such mechanism as the following: In their random thermal motion, solvent molecules continually bounce against the surface of the solute. Solution occurs when solvent molecules carry off solute molecules by clustering about them. A sugar molecule with its associated cluster of water molecules is called a solvated molecule and is believed to move off into solution as a unit. Solvent molecules are continually exchanging places with other solvent molecules in the surrounding area of solvent even though a strong attraction for the solute particle is present. The character of the solvated particles is constantly changing and this tends to make any study of the system difficult.